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THE

PHYSICAL REVIEW

THE DISTRIBUTION OF ENERGY BETWEEN THE MODIFIED AND THE UNMODIFIED RAYS IN THE COMPTON EFFECT

By Y. H. Woo

Abstract

Intensity ratio of modified to unmodified scattered x-rays as a function of scattering angle.—Using small tubes of the Compton type and Soller collimators, reliable measurements of the intensity of scattered x-rays were obtained from five radiators—*paraffin, wood, carbon (graphite), aluminium and sulfur.* An ionization spectrometer (ethyl bromide) with a large calcite crystal was employed. Since the wave-length range investigated was small, the relative energy of each spectrum was obtained, to a close approximation, by integrating with a planimeter the area under the ionization curve which represented the line. The results of this measurement are as follows:

φ	R(paraffin)	R(wood)	R(carbon)	R(aluminium)	R(sulfur)
60°	2.29	1.19	1.08	0.46	....
75	3.10	1.85	1.31	0.74	0.25
90	4.69	2.73	1.45	0.91	0.42
105	5.16	3.21	1.82	1.23	0.67
120	5.49	4.57	2.26	1.45	....
135	6.52	5.38	3.42	2.11	....
150	6.98	6.21	4.05	2.52	....
165	7.47	7.00	4.86	....	....

where φ represents the scattering angle and R the intensity ratio of the modified to the unmodified line. The values of R increase with angle of scattering for a given element in the general manner predicted by Jauncey's theory, but the numerical values given by the theory are 20 to 50 percent too large. For a given angle, the values of R increases as the atomic number decreases, being greatest for paraffin which contains relatively more hydrogen than does wood. Experiments were also performed with a *lithium* radiator kept in a lead cell filled with hydrogen, on which two mica windows (about 0.005 mm in thickness) were provided so that one of them allowed the primary ray to fall on the scatterer and the other permitted the secondary ray to pass into the collimator. With a scattering angle of 110°, the unmodified line was practically absent, certainly less than 4 percent of the modified. This seems to prove that the Compton effect cannot be attributed to anything other than true scattering. This also favors the hypothesis, suggested by A. H. Compton, that the unmodified line occurs when the energy imparted to the electron during the process of scattering is insufficient to eject it from the atom.

IN connection with the study of the Compton effect in the scattered x-radiation it is important to measure the relative intensity of the modified and unmodified lines. Once such measurements have been made with some accuracy, they may throw some light upon the question of how the orbital electrons take part in the scattering effect.

Method and Apparatus

For the measurement of the intensity of the secondary radiation a spectroscopic method was employed. The arrangement of the apparatus was similar in general character to that employed by Compton[1] for measuring the spectrum of the secondary x-rays scattered from carbon and is diagrammatically shown in Fig. 1.

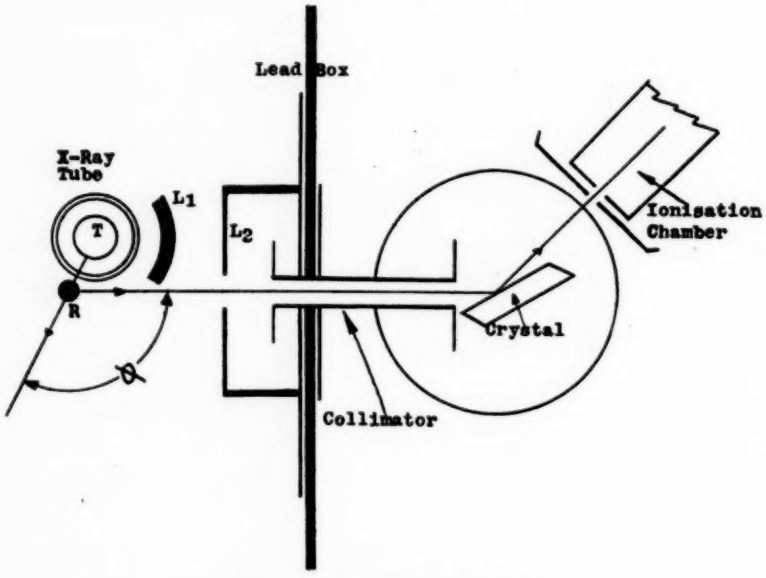

Fig. 1. Diagram of apparatus.

The primary x-rays from the target T of an x-ray tube fell upon the secondary radiator R, which was placed in line with the collimator. Lead screens, L_1 and L_2, disposed between the tube and the collimator, prevented stray radiation from leaving the lead box which contained the x-ray tube. The rays from the secondary radiator R, after passing through the collimator, struck the calcite crystal of the Bragg spectrometer, which reflected some of them into the ionization chamber. A sensitive Compton electrometer measured the ionization in the usual way.

[1] A. H. Compton, Phys. Rev. **22**, 409 (1923).

The collimator, due to Soller,[2] was composed of a pile of sheets of lead foil separated by strips of lead foil. Two collimators, each with a length of about 17 cm, were employed in the present work. The x-ray tube, of small diameter, was of the type described by Compton.[1] For this work a current of 35 to 45 mil-amp. passed through the tube, coming from a generating plant consisting of transformers and kenotrons producing an intermittent direct current at about 65 peak kv. The primary voltage of the high tension transformer was supplied from the mains and was carefully controlled by an induction regulator so that the variation was kept within half a volt.

With these devices, and by using a large calcite crystal to reflect the broad beam from the collimator to the ionization chamber, it was possible to secure sufficient intensity without loss in resolving power. This seems to make a satisfactory apparatus for studying the intensity of the secondary radiation by the ionization method.

Experimental Results

For the study of the energy distribution between the modified and the unmodified rays it was necessary to employ radiators of light elements in order to secure intensity sufficient for precise measurements. In the present experiments paraffin, wood, carbon (graphite), aluminium and sulfur were used as the scatterers. While the samples of paraffin, wood and carbon were in the form of a cylinder 1 cm in diameter, the aluminium and the sulfur were in the form of flat plates. In every case of the first four radiators the spectrum of molybdenum Kα rays was scattered at 60°, 75°, 90°, 105°, 120°, 135°, 150°, and 165° (in the case of aluminum no reliable result was obtained at 165°). Because of an accident to the x-ray tube, the experiments with sulfur were performed only at 75°, 90° and 105°.

One set of the experiments with paraffin as the secondary radiator is represented by Fig. 2, in which the curves represent the inoization current in arbitrary units as a function of the glancing angle of incidence of the rays on the calcite crystal. Curves similar to those in Fig. 2 were obtained for the experiments with wood, carbon, aluminium and sulfur as the radiators. Detailed tabulation of these results would be tedious and unnecessary. For measuring the spctra at 60°, 75° and 90° the width of the slits in the collimator was 0.2 mm, while for 150° and 165° the width of the slits was increased from 0.2 to 0.4 mm in order to secure greater intensity. For 105°, 120° and 135° both collimators were employed at convenience.

[2] W. Soller, Phys. Rev. **23**, 272 (1924).

Two sets of experiments were performed with each of the five samples as the secondary radiator. From these measurements the distribution of energy between the modified and the unmodified lines was estimated. In view of the fact that the wave-length range investigated in the

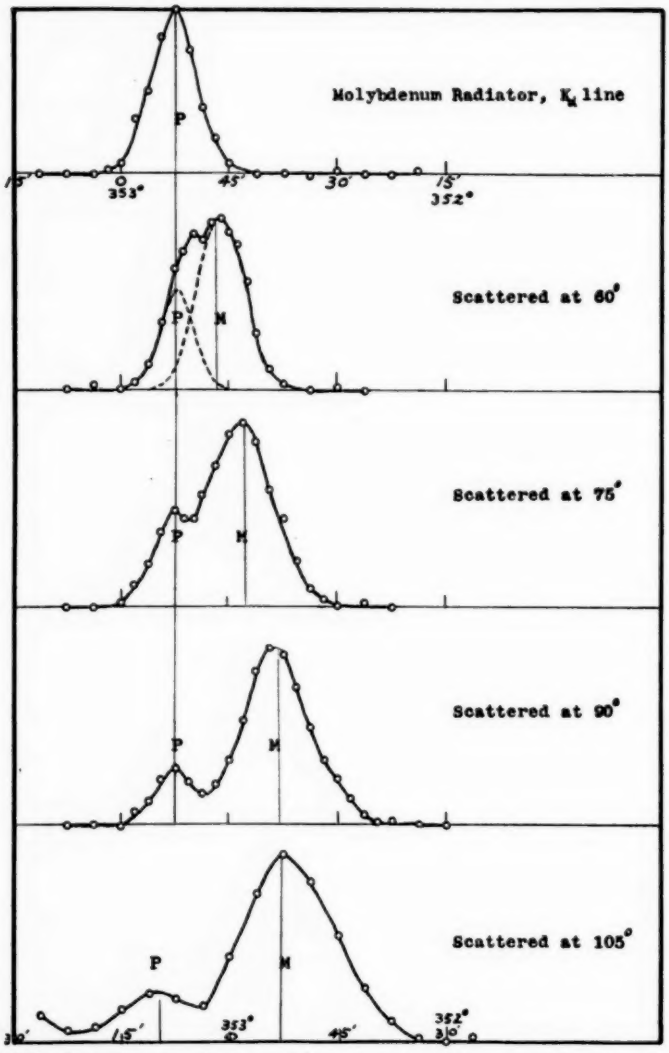

Fig. 2 (A). Intensity distribution of x-rays scattered from paraffin at various angles. *P* marks the position of the primary Mo Kα line, *M* the position of the modified peak calculated from Compton's theory.

present work is small, we can assume to a close approximation that the energy in the different lines is proportional to the area under the ionization curves. This approximation is the more exact since the

reflection coefficient of a calcite crystal is nearly independent of the wave-length, and since the ionization chamber was filled with ethyl bromide vapor and thus absorbed nearly all the x-rays of the wave-length studied. The relative energy of each spectrum was therefore obtained by integrating with a planimeter the area under the curve which represented the line.

Since the modified and unmodified lines were not distinctly separated from each other at 60°, the relative intensity was estimated by resolving the overlapping lines into two parts as shown in the second curve of Fig. 2(A). For measuring the spectra at 165°, the scatterer had to be placed so far away from the target of the tube (about 10 cm) that the measurement was made difficult by the reduction of the intensity of the incident radiation. Thus in the experiment on aluminium the 165° reading was repeated several times without success.

On integrating the area under the peak, attention should be called to the question of drawing the baseline of the ionization curve. It was found that when the collimator with narrow slits (0.2 mm) was employed, the general radiation under both the short wave-length side of the unmodified ray and the long wave-length side of the modified line was usually equally strong and so the line joining the readings of the general radiation is taken as the required baseline. However, when the collimator with wide slits (0.4 mm) was used, the general radiation under the former was always stronger than that under the latter. This was especially so if the scattering angle was large. Since the sensitivity of the electrometer was maintained constant by the use of a sputtered fiber, this effect is considered due to the presence of the modified beta peak. Thus the readings of the general radiation under the modified ray are taken to represent the height of the baseline of the modified and unmodified peaks. The curve representing the unmodified line is then completed to this adopted baseline in such a way that it has the same form as that of the fluorescent molybdenum Kα spectrum as shown in the second curve of Fig. 2(B).

In this connection we may mention the fact, pointed out by Allison and Duane,[3] that the intensity of the unmodified line relative to the general radiation is less in the scattered spectrum than when obtained direct from the target of the tube. This may perhaps be ascribed to (1) the presence of the modified beta peak in the secondary radiation as mentioned above and (2), as suggested by A. H. Compton, the presence of the second order of white radiation, which is excessively

[3] Allison and Duane, Phys. Rev. **26**, 300 (1925).

strong in the scattered rays due to the larger effective scattering volume in the radiator of the shorter wave-lengths. While the first effects depends on both the angle of scattering and the width of the slit, the second varies with the voltage put on the tube.

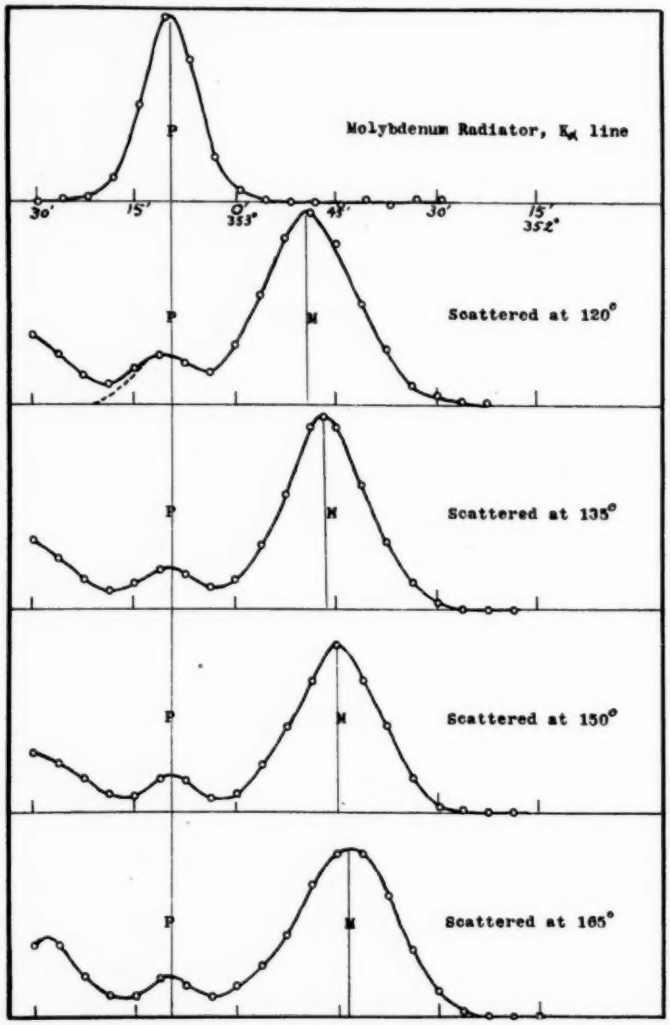

Fig. 2 (B). Intensity distribution of x-rays scattered from paraffin at various angles.

A special series of experiments was also performed by allowing primary rays of different intensities, produced by varying the current passing through the x-ray tube, to fall on a radiator at a definite distance from the target of the tube. It was found that the relative energy in the modified and the unmodified line is within the limit of

experimental error independent of the intensity of the incident radiation.

The results of this measurement of the relative intensities are tabulated in Table 1, where ϕ represents the scattering angle, R the ratio

TABLE I

Ratio of the energy in the modified line to that in the unmodified line for different radiators and various angles

	Wood		Paraffin		Carbon		Aluminium		Sulfur	
	s	R	s	R	s	R	s	R	s	R
60°	0.2	1.19	0.2	2.29	0.2	1.08	0.2	0.46	...	....
75°	0.2	1.85	0.2	3.10	0.2	1.31	0.2	0.74	0.2	0.25
90°	0.2	2.73	0.2	4.69	0.2	1.45	0.2	0.91	0.2	0.41
105°	0.2	3.21	0.4	5.16	0.2	1.82	0.4	1.23	0.2	0.67
120°	0.2	4.57	0.4	5.49	0.2	2.26	0.4	1.45	...	....
135°	0.4	5.38	0.4	6.52	0.2	3.42	0.4	2.11	...	....
150°	0.4	6.21	0.4	6.98	0.4	4.05	0.4	2.52	...	....
165°	0.4	7.00	0.4	7.47	0.4	4.86	...	....	...	....

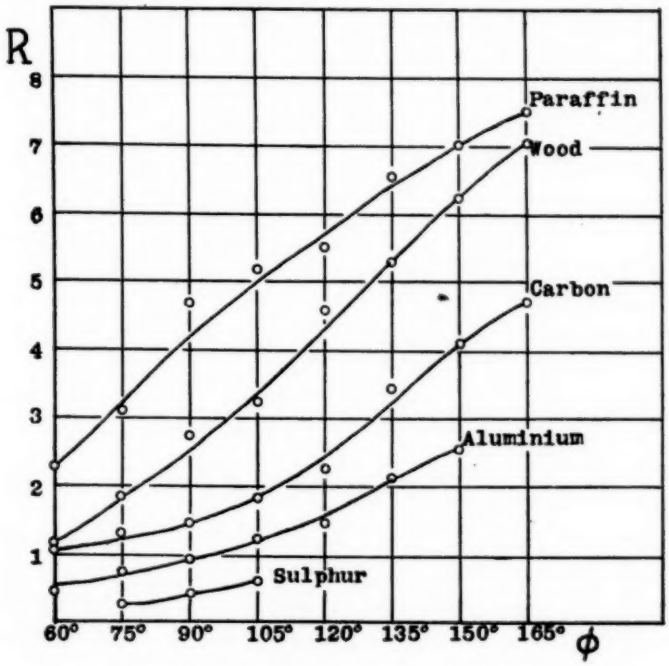

Fig. 3. $R-\phi$ curves for various radiators.

of the energy expressed in arbitrary units in the modified ray to that in the unmodified, and s the width in mm of a single slit in the multiple-slit system.

In Fig. 3 the intensity ratio R is plotted against the scattering angle ϕ. It appears that each set of data approximately fits a smooth curve,

showing the variation of the intensity ratio as a function of the scattering angle. In all cases except for paraffin the experimental curve seems to be concave upward at small angles and convex upward at large ones. As the curve for paraffin is a little irregular, it may be noted that in this case the intensity of the unmodified ray is so small that the electrometer readings are relatively uncertain.

It is worthy of note that the unmodified line in the spectra scattered from graphite is more prominent than that in the spectra scattered from wood, and that in the spectra from paraffin the unmodified ray is particularly faint. Wood is composed of cargon, hydrogen and oxygen, whereas paraffin is a compound of carbon and hydrogen. This clearly indicates that the element hydrogen is most effective in scattering the modified line. In view of the faintness of the unmodified line in the spectra from paraffin it seems probable that the unmodified part of the scattered spectrum is entirely due to the carbon in it. Thus a spectrum scattered from hydrogen would have only the modified radiation. This consideration is supported by the study of the intensity of the secondary rays scattered from lithium, which will be described in the following section.

Intensity of Secondary MoKα Rays Scattered from Lithium

Unpublished results of experiments with lithium as the secondary radiator performed early in May, 1924, by A. H. Compton and the writer showed that, when the lithium sample was freshly prepared, the unmodified line was very faint, though it was undoubtedly present. The same effect has also been noted by B. Davis.[4] Recently Allison and Duane[3] have measured the scattered molybdenum Kα rays from lithium by keeping it from oxidizing with a coating of paraffin oil during the experiments. Their results still indicate the presence of a faint peak at the position of the unmodified line. As pointed out by these authors, their results may have been affected by the scattering from the carbon in the oil.

The writer recently performed a series of experiments by keeping the lithium radiator in a lead cell filled with hydrogen. Two mica windows, 0.005 mm thick, were provided on the lead cell, so that one of them allowed the primary x-rays to fall on the scatterer and the other permitted the secondary radiation from the radiator to pass into the collimator. Since the scattering from lead is negligible and since hydrogen is lighter than lithium, the present experiments were not affected

[4] B. Davis, Phys. Rev. **25**, 737 (1925).

by either of them. Special care was also taken to shield the wax cementing the mica windows.

The results of this measurement are shown in Fig. 4. Curve 1 represents one of the results of the experiments with the lithium sample cleaned in air, while curves 2 and 3 are two of the measurements obtained with the radiator carefully cleaned in an inverted glass jar

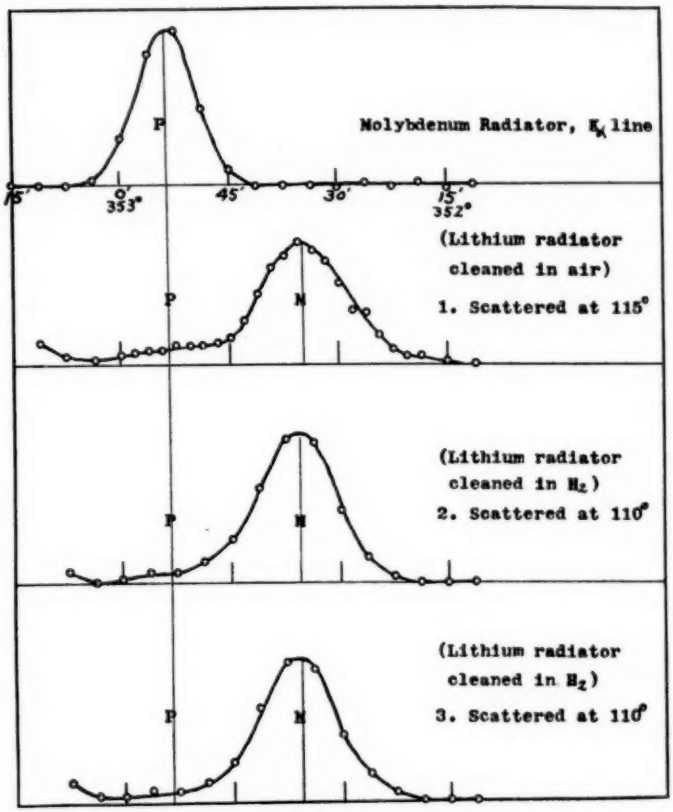

Fig. 4. Scattering from lithium. *P* marks the position of the primary Mo Kα line, *M* the position of the modified line calculated from Compton's theory.

filled with hydrogen. As far as they go, the results indicate that in the secondary x-rays scattered from metallic lithium the unmodified ray in the Compton effect disappears.

Discussion of the Results

The discussion is conveniently divided into two parts: (1) The scattering from all the radiators except lithium and (2) the scattering from lithium.

(1) From results tabulated above it is seen that the energy ratio increases with the scattering angle in the way shown by the curves in Fig. 3. Since the conditions which determine whether an x-ray quantum shall be scattered according to the simple quantum law or in some other manner must also govern the distribution of the energy in the modified and unmodified rays, the present results thus point to the conclusion that the scattering angle should play in some way or other an important role in the determining factors.

A theoretical investigation of the question of the variation in the intensity ratio of the modified to the unmodified ray with angle of scattering for a given element and given incident wave-length has been recently published by Jauncey.[5] The theory requires an increase of the intensity of the modified relative to that of the unmodified line as the angle of scattering is increased. Unfortunately while the agreement between this theory and the present results is qualitative, it is not quantitative. Assuming a resolving power represented by 0.002A, Jauncey[5] gives for the ratio of intensity of modified ray relative to unmodified, 1.74 for carbon at 90° and 0.62 for sulfur at 90°, whilst the present experiments give for this ratio 1.45 for carbon at 90° and 0.42 for sulfur at 90° though the spectrometer arrangement in this work had a resolving power not greater than that corresponding to a wave-length width of 0.004A. This seems to indicate that Jauncey's theory overestimates the relative intensity of the modified and unmodified lines. However, it is of particular interest to note that the curve calculated according to Jauncey's theory to show the variation of the intensity ratio with the scattering angle is of the same general form as that of the curves in Fig. 3 obtained from experiments. This appears to point to the possibility of a further development of Jauncey's treatment.

Finally, it may be remarked that the present experiments also show that for a given angle of scattering the intensity of the modified ray relative to that of the unmodified line decreases as the atomic number of the scatterer increases, and that the width of the modified ray is greater than that permitted by Compton's simple equation. These are in accordance with the results of earlier work done in this field.

(2) From the result of the measurement of the intensity of the scattered radiation from lithium the following conclusions can be readily drawn.

First, it presents conclusive evidence that the Compton effect can not be attributed to anything other than true scattering, and there-

[5] G. E. M. Jauncey, Phys. Rev. **25**, 314 (1925) and Phys. Rev. **25**, 723 (1925).

fore Barkla's idea[6] of differentiating these phenomena is difficult to defend.

Second, it favors Compton's first hypothesis[7] for accounting for the existence of the unmodified rays, that the binding energy of the electron is such that the energy imparted to the electron during the process of scattering is insufficient to eject it from the atom; but it is not quite consistent with his alternative hypothesis that the primary quantum is scattered by a group of electrons instead of a single one. It is also inconsistent with the possible explanation of the origin of the unmodified line that the primary quantum is scattered by the nucleus.

Third, it supports the consideration leading to the conclusion that the spectrum scattered from hydrogen would have no unmodified line.

In conclusion, the writer wishes to express his sincere thanks to Prof. A. H. Compton for his valuable suggestions and ever ready assistance during the course of this work.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
October 23, 1925.

[6] C. G. Barkla, Nature, **114**, 753 (1924).
[7] A. H. Compton, Phil. Mag. **46**, 897 (1923).

THE RELATIVE INTENSITIES OF REFLECTION OF X-RAYS FROM THE PRINCIPAL ATOMIC PLANES OF FLUORITE*

By D. A. MacInnes and Theodore Shedlovsky

Abstract

For these measurements, the usual Bragg apparatus was modified by adding a reference crystal illuminated through the same slit on a line slightly above the other, and a second ionization chamber and Bumstead electroscope. The integrated ionization as the crystal was turned by motor through a given line or range of wave-length was measured. Correction was made for the general radiation. Thus the relative intensities of the Pd α and β lines when reflected from three principal planes of fluorite were determined. The values fall into three groups for each line, each of which fall on a smooth curve when plotted as a function of the angle of reflection, the strongest group being due to Ca and F atoms acting together, a weaker group to Ca atoms alone, and the weakest group to Ca and F planes which are out of phase with each other. Simple quantitative relations between the intensities of these groups have not yet been found, evidently because an additional absorption by the crystal takes place, which varies in an unknown manner with the angle of reflection.

THE investigation to be described below was undertaken in the belief that the accurate determination of the intensities of reflection of x-rays from crystals will yield results which are nearly, if not quite, as important as the determination of the angles of reflection has proved to be. The final decision as to the structures of the more complicated crystals will undoubtedly depend upon exact quantitative determinations of relative intensities of the different orders of reflection from the various planes, in addition to the distances between atomic planes as obtained by measurements of angles. Many examples of the great value of intensity measurements in the determination of crystal structures are given in the work of W. H. and W. L. Bragg.[1] It is also certain that the intensities of reflection are intimately related to the arrangement of the electrons in the atoms.[2]

In the following pages a modification is described of the Bragg apparatus to adapt it to more accurate determinations of intensities. Results are also given of accurate measurements of relative intensities

* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 176.

[1] W. H. and W. L. Bragg, "X Rays and Crystal Structure," Harcourt, Brace and Co.

[2] Bragg, James and Bosanquet, Phil. Mag. **41**, 309 (1921).

of several orders of reflection from the principal atomic planes of fluorite (calcium fluoride).

The Apparatus

The principle of the method for measuring the relative intensities is shown diagrammatically in Fig. 1. The x-rays from the target A pass through the slits S_1, S_2 and S_3 and strike the crystal under observation, C, from which the reflected rays pass to the ionization chamber E under which a Bumstead electroscope, which moves with the chamber, is swung. The crystal and chamber angles are read, in the usual manner, on the graduated scale V. In addition, x-rays which have passed through slits S_1 and S_2, but at a slight vertical angle to the rays which strike crystal C, are intercepted by the crystal C' and are

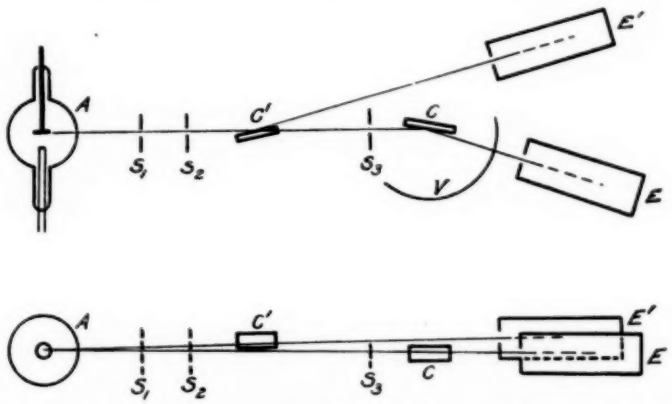

Fig. 1. Diagram of apparatus, showing the arrangement of crystals and ionization chambers.

reflected to the chamber E' which is connected with another Bumstead electroscope. The crystal C' and the chamber E' remain stationary. The electroscopes are calibrated by impressing successive potentials from a potentiometer between the leaves and the ground. The intensities of reflection are therefore found in terms of ratios of the potentials necessary to reproduce the observed deflections of the leaves of the electroscopes. A carborundum crystal C' is used for the reference, as it has a strong second order reflection at a large angle, so that the chamber E' can be placed in such a position that it does not interfere with the chamber E at small angles of reflection. The vapor of ethyl bromide is circulated by a hand operated pump through the chambers E and E' until the same partial pressure of vapor is present in both. It was found necessary to make both chambers gas tight.

This was not found possible with sulfur insulation of the wires leading to the electroscopes, and other insulators, e.g., sealing wax, soon became conducting in the presence of the ethyl bromide. However, a gas tight, perfectly insulating support was formed by using sulfur inside and sealing wax outside. This remained perfect for more than two years.

The Coolidge tube (A in the diagram) was very kindly presented to us by Dr. Coolidge of the General Electric Company. It is air cooled and supplied with a palladium target. It was found necessary to operate this tube continuously while making readings, and for several hours before, since otherwise the position of the target A changes, due to the expansion of the copper rod on which it is supported. The crystals are exposed to the rays simultaneously by moving a lead disk placed between the slits S_1 and S_2. The support of the crystal C' is arranged so that the crystal can be turned through a small angle. The slit S_2 consists of upper and lower halves which can be adjusted separately, making possible independent regulation of the width of the beams hitting crystals C and C'.

The ionization chambers E and E' are 8 in. long and 2 in. in diameter. They are fitted with thin mica windows behind the chamber slits, and with lead glass windows on the other end to aid in the optical adjustment of the crystals.

With this apparatus it is, of course, possible to determine the angles of reflection of the characteristic lines of the palladium spectrum. After locating the exact positions of these reflections from a particular crystal face, the proceedure for determining the relative intensities of the reflections for the α doublet and the β lines and for the various orders of reflection of those lines is as follows. The slit of the chamber E is given a width of 0.5 mm to 1 mm (1 mm = 40′) and adjusted so that the center of the slit is at the maximum of reflection for the line. Then the crystal C is rotated slowly (by means of an electric motor and a worm gear) through one degree, half of which lies on either side of the maximum of reflection in question. For a check measurement the crystal is then turned in the opposite direction through the same range. The time of rotation is regulated so that sufficient radiation has entered the ionization chambe s to give large enough deflections of the electroscope leaves for an accurate measurement. For the weaker lines deflections from several rotations are allowed to accumulate in the electroscope connected with E, whereas the electroscope for E' is grounded before each reversal of the motion and a record is made of the sum of the successive deflections. In this way the intensities of the weaker lines

are obtained with nearly as great accuracy as for the stronger ones. Besides the α and β characteristic radiations, this procedure involves reflection into the chamber of general radiation. A correction for this is made by obtaining a complete series of measurements on reflections at angles at which reflections of characteristic rays do not take place. It is then possible to draw smooth curves through the resulting points, and to find accurate values of the reflection of general radiation at angles at which characteristic reflection also takes place. These curves for general radiation indicate the structure of each crystal face in much the same manner as is done by the characteristic radiation. For instance, the (100) face of fluorite, which has a strong second and fourth order and almost no first and third order reflections, showed the same peculiarities in reflection of general radiation, maxima and minima of this reflection occurring on a smooth curve, at points corresponding to even and odd order reflections.

We have given considerable attention to the effect of the state of the crystal surface on the resulting reflection, and have found, as has been observed by Bragg and his associates[2] and by Dickinson,[3] that the most reproducible results are obtained from crystal surfaces that have been ground or roughened. In this work the (100), (110) and (111) faces were studied. Of these the first and last occur naturally and the second had to be ground artificially. Irregularities due to grinding were largely overcome by inverting the crystal after a series of measurements and repeating, and then averaging the result of the two sets of measurements. In this procedure we followed the suggestion of Bragg, James and Bosanquet.[2]

After determining the relative intensities for the different orders of reflection for the three principal planes it was necessary to bring these three sets of ratios to the same scale. This was done by observing the integrated effect in the electroscope of swinging each of the crystal faces through an angle large enough to include the α doublet and the β lines, and a certain amount of general radiation. The angle was chosen so as to include the same range of general radiation for each face. In this way the (200), (111) and (220) intensities were found to be in the ratios: 1.00, 2.47, 0.487.

In these measurements much use was made of the photographic method for locating reflections. The images on the films gave definite information as to whether the crystal was reflecting completely or only partially into the chamber slit. The orientation of the crystal with the

[3] Dickinson and Goodhue, J. Am. Chem. Soc. **43**, 2046 (1921).

purpose of excluding reflections from other planes than the one under measurement was also made possible by that method.

The Experimental Results

A summary of the results is given in Table I. All the intensities are given with reference to that of the (100) reflection which has arbitrarily been given the value 100.

Table I

The relative reflections of characteristic palladium rays from fluorite

Line	Angles		Relative intensities	
	α	β	α doublet	β
100	6°10′	5°26′	0.53	0.17
200	12°24′	10°55′	52.8	18.3
300	18°48′	16°30′	0.40	0.20
400	25°26′	22°15′	7.92	3.39
110	8°38′	7°37′	100.0	33.2
220	17°27′	15°22′	25.7	9.31
330	26°45′	32°25′	6.67	3.23
111	5°19′	4°42′	130.3	42.1
222	10°41′	9°25′	1.15	0.51
333	16° 9′	14°12′	16.2	5.73
444	21°46′	19° 6′	13.3	5.33

The ratios given in this table were determined as described above with the exception of the two values given for the (111) reflection. In that case the angle of reflection was so small that a separation of the α doublet from the β line for the purpose of measuring intensities was not possible, though the "peaks" were, of course, easily measured. To overcome this difficulty a measurement of the sum of the intensities of the α and β reflections was made, and an estimate (by methods to be described) was obtained of the ratio of the two, from which the results in the table were computed. The measurement of the sum of the intensities was carried out by widening the chamber slit and swinging the crystal through a larger angle than in the determinations of the intensity of a single reflection. The ratio of the α to the β reflection for this line was then estimated in two different ways. First a short extrapolation was made of a curve in which the ratios of the α to the β intensities of all the stronger reflections were plotted against the mean angle of reflection. From the resulting smooth curve to the mean angle of the (111) reflection gave the ratio 3.08. Secondly, it was found that for the more intense reflections a straight line was obtained, for both the α and the β series, when the intensities were plotted against the inverse sine of the angle of reflection. A short extension of these two lines to angles corresponding to the (111) reflections yielded values in the ratio of 3.09, which was adopted for the figures in the table.

Discussion of the Results

A plot of all the data in Table 1 is shown in Fig. 2 in which the square roots of the relative intensities are plotted against the reciprocal sines (cosecants) of the corresponding angles. For the α doublet reflections there are two curves connecting a series of points, and also two isolated points which are connected in the figure by dotted lines. For the β series there is a completely analogous series of lines and points. As plotted all the curves tend to converge toward a zero of intensity at a value of the abcissa of unity, i.e., an angle of 90°. Similar smooth

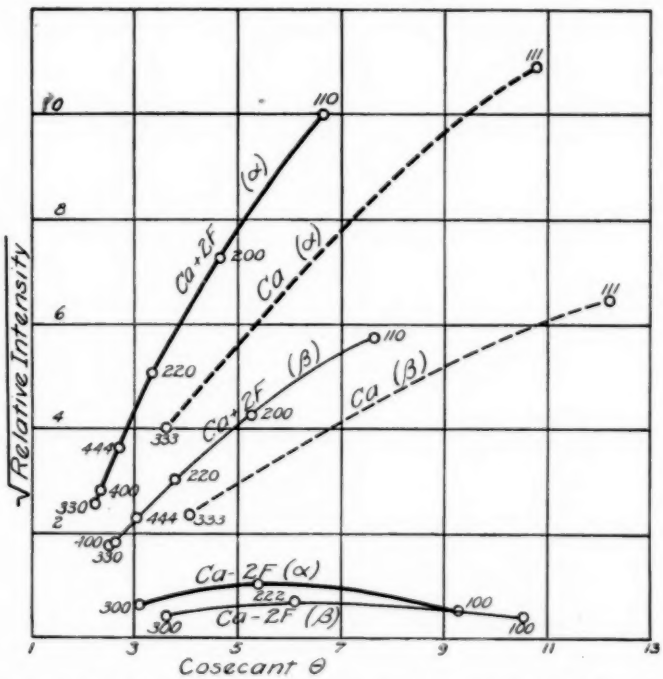

Fig. 2. Variation of the square root of the relative intensities with the cosecant of the corresponding angles.

curves connecting the intensity of reflection with a function of the angle of reflection have been found by Bragg and Bragg[1] and by Bragg, James and Bosanquet[2] for sodium chloride, and by W. H. Bragg[5] for diamond. The angles and intensities observed are in complete accord with the structure for fluorite proposed by Bragg and Bragg.[1] According to their analysis the arrangement of atoms in the various planes of the crystal is as shown in Fig. 3 in which the solid lines represent planes containing calcium atoms and the dotted lines planes of fluorine atoms. In the cubic (100) faces, planes of calcium atoms alternate

with planes of fluorine atoms. This results in interference in the rays from alternate planes for odd orders of reflection, and reinforcement for even orders. Since the number of electrons in the calcium atom (20) is very close to that for the two fluorine atoms (18) the interference is nearly but not quite complete. (The numbers are the same, but interchanged, if the atoms are present as charged ions.) The planes of the prism (110) faces contain both calcium and fluorine atoms, and all the planes being alike the normal order of decrease of intensity for the various orders is observed. This decrease is 100, 25.7, 6.7 for the α doublet and 100, 28.0, 9.6 for the β reflections. The octahedral (111) planes are of somewhat more complicated character. Here in the distance d between the planes of calcium atoms, two planes of fluorine atoms are present, both spaced $d/4$ from the former planes. The result of this "quartered" arrangement is that the first order of reflection is due to the calcium planes only, since the rays from the two sets of

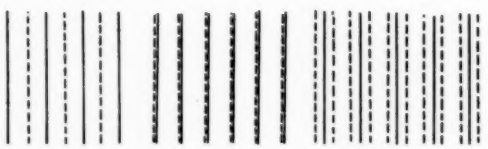

Fig. 3. The arrangement of the atoms in the various planes of the crystal of calcium fluoride according to W. H. and W. L. Bragg. The solid lines represent planes containing calcium atoms and the dotted lines planes containing fluorine atoms.

fluorine planes are exactly out of phase with each other. On account of the small angle of reflection this intensity is higher than any of the others although due to scattering from only a portion of the atoms. In the second order (222) the reflection from the calcium planes is in opposition to the fluorine planes, and is thus similar to the (100) and (300) reflections. The third order (333) is similar to the (111), but for the (444) all the trains of waves are in phase and reinforce.

The reflections divide naturally into three groups: (a) those from mixed planes and those in which the waves from the calcium and fluorine planes are in phase (these form the curves marked Ca+2F in Fig. 2), (b) reflections from calcium alone, which are shown in the figure by points connected by dotted lines, and (c) reflections in which the fluorine planes are in opposite phase to the calcium planes, indicated by curves marked Ca-2F in the figure. It is interesting to note that the different orders of reflection from the octahedral (111) face contribute to all of the groups, and also that the Ca+2F curve contains

points from the three planes measured. Bragg and Bragg did not report any of the reflections in group (c), but that for (100) has, however, been observed by Pealing.[4]

It would appear at first sight that it should be easy to compute values of intensity in any one of the groups (a), (b) and (c) from data given in the other two groups. This has not, however, been found to be the case. The reflections from calcium, for instance, which involve about half of the electrons have considerably more than half the intensity (at corresponding angles) of the reflections from planes involving all the electrons in the molecule. Quantitative agreement between the values in the different curves is, however, more nearly approached as the intensities decrease. A similar result, for diamond, has been observed by W. H. Bragg.[5] The phenomenon is undoubtedly due to an additional absorption, or extinction, of the x-rays at angles at which reflection takes place. A further discussion of this subject, and of the applicability of the Darwin-Compton equation for x-ray intensities to our results, will appear in another paper.

The authors wish to acknowledge the efficient assistance of Mr. Eric Townsend.

RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
November 25, 1925.

[4] Pealing, Proc. Phys. Soc. London, **33**, 297 (1921).
[5] W. H. Bragg, Proc. Phys. Soc. London, **33**, 304 (1921).

K-SERIES EMISSION SPECTRA FOR THE ELEMENTS FROM TA(73) TO BI(83)

By B. R. Stephenson and J. M. Cork

Abstract

The specially designed water-cooled tube enabled currents of 8 milliamp. at 150 kv to be used. By connecting the same rheostat in the primaries of both high-tension and filament transformers, irregularity due to hot spots on the target was automatically smoothed out. An automatic electromagnetic cutout prevented excessive current when gas developed. With these arrangements, accurate measurements were made of the K-lines for all elements from Ta(73) to Bi(83) excepting Hg, the elements being placed in sheets or layers on the thin copper target. The $\sqrt{\nu/R}$ values plotted as a function of atomic number give practically straight smooth curves, as is to be expected. The differences in the ν/R values for the α and α' lines agree well with the corresponding values for $L\beta$ and $L\alpha'$. The corresponding wave-length differences are nearly constant and equal to 4.85.

UNTIL very recently the only two elements of the group from Ta(73) to Bi(83) for which the K-series emission wave-lengths had been measured were tungsten and platinum. Duane and Stenstrom,[1] Siegbahn,[2] Cork,[3] Lilienfeld and Seeman,[4] DeBroglie,[5] and Rogers[6] have measured one or both of these elements. Just recently Rechou[7] has published measurements on the elements from tantalum to uranium.

Apparatus

The spectrometer was of the type used by one of us in a previous investigation but was made larger. The distance between the second slit and the photographic plate was 75.593 cm. This gave a much larger separation of the lines on the plate. The plate holder was a rectangular frame machined out of one piece of solid brass and set optically perpendicular to the axis of the spectrometer. The photographic plate was held against the back face of the plate holder by three springs so that the emulsion side of the plate which faced the slit

[1] Duane and Stenstrom, Proc. Nat. Acad. **6**, 477 (1920).
[2] Siegbahn, Spectroscopy of X-rays, p. 104 (1925).
[3] J. M. Cork, Phys. Rev. **25**, 197 (1925).
[4] Lilienfeld and Seeman, Phys. Zeit. **19**, 269 (1918).
[5] DeBroglie, Comptes Rendus **169**, 134 (1919).
[6] Rogers, J. S., Roy. Soc. Victoria, Proc. **34**, 136.
[7] Rechou, M. G., Comptes Rendus **180**, 1107 (1925).

system was always the same distance from the second slit. X-rays were allowed to fall only on one side of the crystal at a time, thus giving all of the lines of the K series on one side of the plate simultaneously; the other half of the photographic plate being covered by a lead plate to prevent fogging during this time. The crystal was calcite and about 3 mm thick.

The x-ray tube was made with the target and filament removable at ground joints which were sealed with stopcock grease. The total tube length was about 18 inches, with the removable target 8 inches long and the ground stopper for the filament leads about 6 inches long. The target was of special design with two compartments so arranged that the part of the target which was in contact with the ground joint was always filled with the inflowing cold water while the heated water from the hot end of the target was carried by a tube through the center of the outer compartment and thus did not heat the joint. This enabled the use of tube currents as large as 6 to 8 milliamp. at 150 kv when elements with a high melting point were being used on the target. The filament was a spiral form of tungsten wire held in the filament container of a regular Coolidge tube which had been adapted to this apparatus. The lead wires were sealed in the outer end of the stopper to prevent puncturing such as often happened when the wires were sealed in at the inner end of the stopper. As both ends of the tube were different in potential from ground by half of the applied voltage, the leak through the target cooling water to ground was very large. With 55 feet of quarter-inch continuous glass tubing well insulated from ground the leak was from 6 to 7 milliamp. at the highest voltages.

The pumping system consisted of a two-stage mercury vapor pump with liquid air trap, backed by a rotary oil fore-pump. When the pumps and tube were working well, an x-ray vacuum could be obtained in about two or three hours. The time was shorter for the lower voltages.

The potential for the tube was obtained from a Victor Special 200 kv transformer and mechanical rectifier. The filament current was supplied by a Victor filament transformer. The voltage was regulated by means of an autotransformer and a rheostat in series with the primary of the high tension transformer.

Under ordinary conditions the tube current was unsteady, due to hot spots being produced on the target when some small bit of the powder became slightly detached from the target or when the sheet metals became slightly loosened and melted. This was overcome by

using the same rheostat as part of the resistance of both the high tension primary and the primary to the filament transformer. Thus when the tube current tended to increase, the fall of potential over this common part of the resistance was increased and the filament current thereby diminished. This stabilizer held the current very steady as long as the voltage remained constant.

An electromagnet was placed with its exciting coil in parallel with the primary of the high tension transformer, and arranged to hold the primary circuit closed. When gas developed in the tube, as often happened, the tube current increased very much, causing the potential difference at the terminals of the high tension primary to fall; this allowed the electromagnet to open and thus break the circuit. The electromagnet was very quick acting and saved the tube as well as the rest of the apparatus from overheating. With these two devices it was possible to leave the apparatus for an indefinite period without fear of injury. A clock attached to the arm of the electromagnet was arranged to stop when the circuit was opened so that the time of exposure could be accurately determined. It was found that about 10 milliampere-hours at the proper voltage were necessary to give a strong exposure. The potential used varied from 120 kv for Ta to 156 kv for Bi.

All of the elements were obtained in as pure a form as possible. Tantalum, platinum, and gold were in sheets and were held on the face of the target. Platinum and gold were soldered to the copper face while tantalum, which could not be soldered, was wedged into a groove in the target. Osmium and irridium were powdered and rubbed onto the target. Two or three applications of the powder for each plate were sufficient. Thallium, lead and bismuth were flowed onto the target like solder. With all the elements, and especially with the last three, considerable difficulty was experienced because of the intense heat melting the element and sputtering the walls of the tube, causing it to puncture. It was not possible to get any of the elements in sufficiently good thermal contact with the target to avoid melting and sputtering. The face of the target was only about 2 mm thick and was made of copper to conduct the heat better and yet the high melting point metals became white hot at the focus. Since thallium, lead, and bismuth have such low melting points a very small tube current had to be used to avoid excessive sputtering. The tube was often taken down and cleaned, for it punctured easily if the walls became coated with sputtered metal.

Measurements and Accuracy

This investigation was carried out in the second basement of the new Physics building where the temperature varied not more than 2°C at any time and usually not more than one degree. The plates and the length of the spectrometer were measured at the same temperature thereby eliminating any temperature effects. The length of the spectrometer was measured with a "Starrett" micrometer scale capable of measuring to 76.5 cm. This measurement was checked by making a rod with an adjustable end piece which could be set at the exact length between the slit and the plate and then measured on the same comparator as that used in measuring the plates. Grooves were filed out of the rod down to the center so that the rod could be measured in steps without having to change the focus of the telescope.

A distance of .25 mm on the plate corresponded to 1 x-unit and since the plates could be measured to 0.01 mm with a Gaertner comparator the measurements are certainly accurate to 0.1 x-unit. Four different crystals were used during the course of the investigation but no appreciable difference was observed in the values for the tungsten lines obtained.

Results

Table I gives the values of the wave-lengths obtained. The values for tungsten obtained by one of us[3] previously, corrected for an error in the micrometer scale, as well as those of Duane and Stenstrom and Siegbahn are included for comparison. All of these values are corrected where necessary for any differences in the value of the crystal grating constant. The values obtained by Rogers[6] for platinum are also included.

Table I

Wave-length values in x-units of K series lines

Element	α'	α	β	γ	Investigators
73 Tantalum	219.73	214.88	189.91	184.52	Present
74 Tungsten	213.45	208.62	184.22	178.98	Present
	213.48	208.67	184.28	179.07	Duane and S.
	213.45	208.60	184.35	178.87	Cork
	213.52	208.85	184.36	179.40	Siegbahn
76 Osmium	201.31	196.45	173.61	168.75	Present
77 Iridium	195.50	190.65	168.50	163.76	Present
78 Platinum	190.04	185.23	163.70	158.87	Present
	189.54	185.11	164.37	159.55	Rogers
79 Gold	184.83	179.96	159.02	154.26	Present
81 Thallium	174.66	169.80	150.11	145.39	Present
82 Lead	170.04	165.16	146.06	141.25	Present
83 Bismuth	165.25	160.41	142.05	.....	Present

Since the temperature of the laboratory remained practically constant at 22°C the value of the grating constant given by Siegbahn[2]

log $2d = 0.78235$ was used. No correction is made in the values of Table I for the effect of the refraction of the x-rays by the crystal. The magnitude of this correction is indicated by the following equation, $\lambda = 2d\ (1 - 0.000135) \sin\theta$. Thus the α line of tantalum 214.88 would become 214.85 x-units.

In Table II are given the frequency values ν/R, where ν is the reciprocal of the wave-length expressed in angstrom units and R is the Rydberg constant 109,737. These values are proportional to the energies emitted when the corresponding electron shifts occur.

TABLE II

ν/R values of K series lines

Element	α'	α	β	γ
73 Tantalum	4147.3	4240.8	4798.6	4938.6
74 Tungsten	4269.2	4368.2	4946.7	5092.4
76 Osmium	4526.7	4638.8	5249.0	5409.4
77 Iridium	4661.4	4779.8	5408.1	5564.7
78 Platinum	4795.9	4919.9	5566.8	5731.9
79 Gold	4930.2	5063.9	5730.5	5907.4
81 Thallium	5217.4	5366.8	6070.6	6267.9
82 Lead	5359.4	5517.8	6239.1	6451.3
83 Bismuth	5514.6	5680.9	6415.3	.....

Table III gives the values of the square root of the frequency terms, $\sqrt{\nu/R}$. When these values are plotted with atomic number the curves shown in Fig. I are obtained. These points, shown by circles, fall very closely on smooth curves. The vaues obtained by Réchou, when they differ enough from our values to be indicated separately, are indicated by crosses. It is evident that some of his measurements show large deviations.

TABLE III

$\sqrt{\nu/R}$ values of K series lines

Element	α'	α	β	γ
73 Tantalum	64.40	65.12	69.27	70.28
74 Tungsten	65.34	66.09	70.33	71.36
76 Osmium	67.28	68.11	72.47	73.49
77 Iridium	68.28	69.14	73.54	74.62
78 Platinum	69.25	70.14	74.61	75.71
79 Gold	70.22	71.16	75.70	76.88
81 Thallium	72.23	73.26	77.91	79.17
82 Lead	73.21	74.28	78.99	80.32
83 Bismuth	74.26	75.37	80.10	.....

Table IV gives a comparison of the differences of the frequency values ν/R for the $K\alpha'$ and $K\alpha$ lines shown in column 2, and the results obtained by taking the frequency differences of the $L\alpha'$ and the $L\beta$ lines which represent the same energy differences, shown in column 3. The two columns agree fairly well. The values obtained by Réchou are also shown in column 4. In column 5 is given the wave-length difference ($\Delta\lambda$) between the $K\alpha'$ and $K\alpha$ lines. This wave-

length difference for the relativity doublet is nearly constant for elements of large atomic number.

TABLE IV

Doublet differences

Element	$\Delta(\nu/R)$ $K\alpha'-K\alpha$ Our data	$\Delta(\nu/R)$ $K\alpha'-K\alpha$ Rechou	$\Delta(\nu/R)$ $L\beta-L\alpha'$	$\Delta\lambda$ $K\alpha'-K\alpha$ (x-units)
73 Tantalum	93.5	96.8	92.7	4.85
74 Tungsten	99.0	100.6	98.5	4.83
76 Osmium	112.1	105.7	111.1	4.86
77 Iridium	118.4	113.0	118.6	4.85
78 Platinum	124.0	117.7	125.9	4.81
79 Gold	133.7	140.3	135.6	4.87
81 Thallium	149.4	172.3	150.5	4.86
82 Lead	158.4	158.9	160.0	4.88
83 Bismuth	166.3	164.7	169.7	4.84

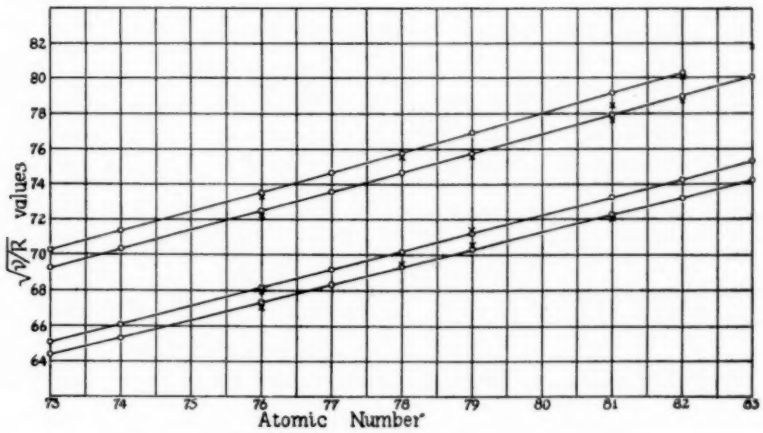

Fig. 1. $\sqrt{\nu/R}$ values as a function of atomic number.

The β line in every case appears much wider than the α' and the α lines, thereby indicating that it is complex. On some plates the components β and β' were sufficiently well defined to be separately measurable, but these are not recorded.

The x-ray tube was made of Pyrex glass which is supposed to be free from lead, but on every plate set for the measurement of short wave-lengths the lead K absorption edge appeared. This cut off completely the γ line of bismuth even though the α', α and β lines appeared very black.

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UNIVERSITY OF MICHIGAN,
October 24, 1925.

STRIPPED OXYGEN, O_{VI}, THE PP′ GROUP IN O_V, AND NEW ALUMINUM LINES IN THE EXTREME ULTRA-VIOLET

By I. S. Bowen and R. A. Millikan

Abstract

Lines of stripped oxygen O_{VI} and of O_V.—The oxygen atom holds its last electrons so tenaciously that hitherto no lines assignable to stripped oxygen have been obtained. Using aluminum electrodes and high resolution, the "lithium doublet" of stripped oxygen has been definitely located at 1031.98, 1037.69A (see Plate I) the component of shorter wave-length being, as usual with this doublet, the more intense. The use of pure Al electrodes has also enabled the pp' group of O_V to be obtained in the fourth order, definitely resolved as a sextuplet (see Plate II) the ratio p_1p_2/p_2p_3 coming out 2.27, reasonably close to the value 2 called for by Lande's interval rule.

New aluminum lines between 1250 and 500A.—Fifteen new faint lines have been discovered and all definitely placed in their proper series, belonging to Al_{III} and Al_{II}.

Ionization potentials of stripped atoms.—Extrapolation from the known values for stripped atoms in the first and second rows of the periodic table, gives values for the $2s$ term which correspond to the following ionization potentials: for N_V 97.39; for O_{VI} 137.35; for F_{VII} 184.07; and for Cl_{VII} 113.73 volts. These are probably accurate to within 0.2 volt.

1. Stripped Oxygen

IN preceding work we have been able to strip off completely the valence electrons from all of the elements contained in the first two rows of the periodic table[1,2,3] save only oxygen and fluorine. These two atoms hold the last of their valence electrons more tenaciously than do any of the others—the quantitative analysis follows later—and would therefore be expected to be the most difficult to reduce to the stripped condition.

In our earlier plates we sought for evidences of the stripped oxygen atom (O_{VI}) without finding any lines which could be unambiguously assigned to it. Since we have been using a very narrow slit and high resolution, some of our plates have revealed two faint but very definite lines which we can now obtain in both first and second order spectra and which, as is conclusively proved below, constitute the "lithium-doublet" of stripped oxygen.

[1] Millikan and Bowen, Nature, **114**, p. 380 (1924).
[2] Bowen and Millikan, Phys. Rev. **24**, p. 209-222 (1924).
[3] Bowen and Millikan, Phys. Rev. **25**, p. 295-305 (1925).

These lines come out best when the electrodes used are pure aluminum, rather than salt-impregnated cores, for the latter tend to lower somewhat the vacua and especially the potentials to which the tips of the electrodes are raised before the spark occurs. It may be remembered that we have shown previously[4] that so-called "chemically pure aluminum" furnished primarily the oxygen spectra between 250A. and 1300A. The two new oxygen lines are shown in Plate I. Their measured wave-lengths are shown in Table I.

TABLE I

Lines of stripped oxygen O_{VI}

Intensity	λ I.A. Vac.	ν	$\Delta\nu$	Series designation
1	1031.98	96901.6	533.8	$2s-2p_1$
0	1037.69	96367.8		$2s-2p_2$

When the frequency ν and the frequency-separation $\Delta\nu$, corresponding to these two lines are subjected to the test of the regular and irregular doublet-law-progressions with atomic number, such as we have brought to light in preceding papers[2,5] there result Tables II and III,

TABLE II

Regular L doublets, one-electron systems

$2p_2-2p_1$

Element	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.365}$	s
Li_{II}	.338	.981	2.019
Be_{III}	6.61	2.063	1.937
B_{IV}	34.4	3.116	1.884
C_V	107.4	4.142	1.858
N_{VI}	259.1	5.162	1.838
O_{VII}	533.8	6.184	1.816

TABLE III

Irregular L doublets

$2s-2p_2$

Element	$\Delta\nu$	Diff.	2nd Diff.
Li_{II}	14903.8		
		17023.8	
Be_{III}	31927.6		592.7
		16431.1	
B_{IV}	48358.7		308.6
		16122.5	
C_V	64481.2		148.6
		15973.9	
N_{VI}	80455.1		61.2
		15912.7	
O_{VII}	96367.8		

respectively. The perfect fitting of these two lines into both these tables removes all uncertainty as to the correctness of their identifica-

[4] Millikan and Bowen, Phys. Rev. **23,** p. 1-34 (1924).

[5] Bowen and Millikan, Phys. Rev. **26,** p. 310-318 (1925).

tion as the "lithium doublet" lines of stripped oxygen (O_{VI}). It will be noticed, also, from a glance at Plate I that these lines follow the rule which also holds for this lithium doublet that the component on the short wave-length side is the stronger.

2. Ionizing Potentials of Stripped Atoms

The excitation of the O_{VI} atom from which these lines originate requires the highest energy of any optical series with which any one has thus far worked. The ionizing potentials of all the stripped atoms of the first row of the periodic table may be easily computed. Since the inmost p orbits of all the stripped atoms of the elements of this row are circular, for in this row they are $2p$ orbits, the progression of their terms and convergence frequencies with atomic number will follow closely the square law of the simple Bohr theory, i.e., the frequency of the $2p$ term of O_{VI} must be nearly 6^2 times that of lithium. More accurately, the study of the empirical progression of the value of

$$Z-\sigma=\sqrt{\nu n^2/R} \tag{1}$$

for the $2p_1$ term of the series of stripped atoms from Li through C yields, as previously pointed out by us,[1] the first four numbers of Table IV. The results of our extrapolation with the aid of these four values to corresponding values for N, O and F is shown in the last three numbers of the second column of Table IV. These numbers could scarcely be in error by as much as .005, which would correspond to not

Table IV

Ionization potentials of stripped atoms

Element	$2p_1$	Diff.	Ionization Potential	λ^{2s}
Li_{II}	1.02074			
		.02620		
Be_{III}	2.04694			
		.01707		
B_{III}	3.06401			
		.01056		
C_{IV}	4.07457			
		.00640		
N_V	5.08097		97.39	126.75
		.00381		
O_{VI}	6.08478		137.35	89.88
		.00224		
F_{VII}	7.08702		184.07	67.07

more than 0.2 volts in the resulting ionization potential. Computing from the foregoing formula the values of ν corresponding to these values of $Z-\sigma$ and then adding the frequency given in Table III of the $(2s-2p_1)$ line gives the frequencies of the $2s$ terms. These correspond to the ionization potentials shown in the fourth column of Table

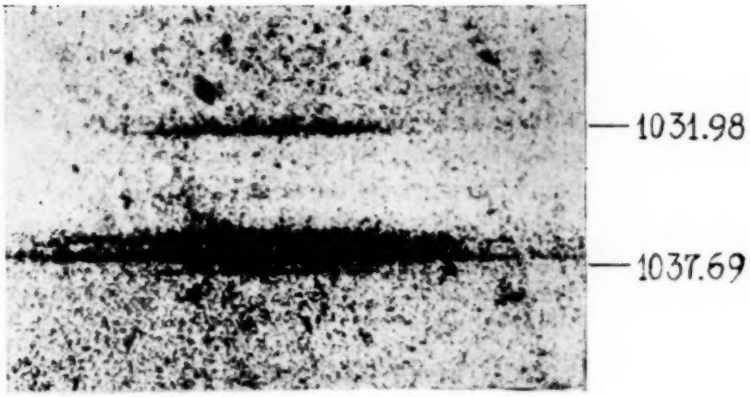

Plate I. The "lithium doublet" lines of stripped oxygen (O_{VI}).

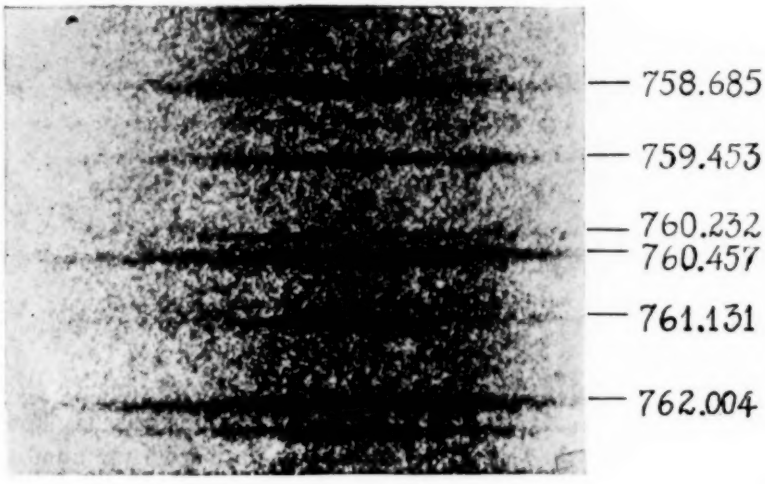

Plate II. The *pp'* group of stripped oxygen (O_V).

IV. The corresponding convergence wave-length of the principal series is given in the fifth column.

By a similar procedure the highest ionizing potential of any stripped atom of the elements in the second row of the periodic table, viz: that of chlorine (Cl VII), is found to be 113.73 volts. The corresponding value for sulfur is 87.6 volts, as we have previously shown.[3] It is obvious that the higher the value of this ionizing potential the more rapidly will the atom when once stripped begin to regain its valence electrons and hence the less the chance that it will be found emitting in the stripped state. This explains why the lines corresponding to stripped oxygen are more difficult to bring out than those corresponding to sulphur or even to chlorine.

3. The pp′ Group in O_V

The added sharpness and strength with which the O_{VI} and O_V lines come out when pure aluminum is used as electrode material has recently enabled us to obtain the pp' group in O_V in the fourth order spectrum where the resolution is so excellent that all of its six components are clearly separated, as is shown in Table V. This separation makes it

TABLE V

pp′ Group in two-valence electron oxygen O_V

	p_1		p_2		p_3
Int. :			(4)		
λ :			761.131		
ν :			131383.4		
$\Delta\nu$;			155.4		
Int.	(4)		(3)		(4)
λ :	762.004		760.232		759.453
ν :	131232.9	305.9	131538.8	134.9	131673.7
$\Delta\nu$;	267.0		268.2		
Int. :	(5)		(4)		
λ ;	760.457		758.685		
ν ;	131499.9	307.1	131807.0		

possible to obtain, for the first time among the two valence electron atoms of the first row of the periodic table except Be (already known), the value of the ratio p_1p_2/p_2p_3. As may be seen from the numbers in Table V, the ratio comes out 2.27, in much closer agreement with the value 2 called for by Lande's interval-rule than is Be, which quite anomalously has the value[6] 3.57. Plate II shows the pp' group in O_V in the fourth order, with all of the six components definitely resolved and labelled.

[6] Sommerfeld, Atombau und Spektrallinien, 4th ed., p. 661.

4. New Aluminum Lines in the Extreme Ultra-violet

In our former cataloguing of extreme ultra-violet lines we listed[4] but two lines between 1250A and 500A as certainly belonging to aluminum, viz., 859.9 and 695.9, and these of intensity 0 and 1, respectively. On our new plates we have been able to bring out these lines with greater intensity and resolution, and to cause fifteen other faint lines to appear, as shown in Table VI. All save four of these lines were

TABLE VI

Series lines of aluminum, Al_{II} *and* Al_{III}

Intensity	λ I.A. Vac.	ν	Series designation	Stage of ionization
0	560.24	178494.9	$3s-5p$	III
3	695.82	143715.3	$3s-4p_1$	III
2	696.23	143630.7	$3s-4p_2$	III
0	725.74	137790.4	$3p_2-6s$	III
0	726.95	137561.0	$3p_1-6s$	III
3	854.98	116961.8	$3p_2-5s$	III
3	856.80	116713.4	$3p_1-5s$	III
1	892.00	112107.6	$3p_2-4d$	III
1	893.93	111865.6	$3p_1-4d$	III
0	1048.83	95344.3	$3p_2-5d$	II
0	1050.01	95237.2	$3p_1-5d$	II
0	1162.59	86014.8	$3d-6f$	III
1	1189.07	84099.3	$3p_3-4d$	II
2	1190.07	84028.7	$3p_2-4d$	II
2	1191.83	83904.6	$3p_1-4d$	II
0	1209.25	82695.9	$3p_3-5s$	II
1	1210.12	82636.4	$3p_2-5s$	II
1	1211.93	82513.0	$3p_1-5s$	II

predicted by Paschen,[7] his predicted values differing from our observed values only by a few hundredths angstroms, which is as close agreement as could be expected when we are working with lines so faint that they cannot be obtained in orders higher than the second.

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CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA,
November 4, 1925.

[7] Paschen, Ann. d. Physik, **71**, p. 142-161, 537-561 (1923).

THE ABSORPTION SPECTRUM OF TIN VAPOR IN THE ULTRAVIOLET

By R. V. Zumstein

Abstract

Spectrum of tin.—(1) *Arc spectrum.* The spectrum of a 25 ampere arc was measured between 2170 and 1950A and 12 new lines observed. (2) *Absorption spectrum of tin vapor, 6000 to 2000A.* The tin was heated in a small carbon tube to about 1600°C and 53 absorption lines were observed, of which 38 are new. (3) *Frequency differences.* The results in general support the table of frequency differences given by McLennan, Young and McLay, lines from the normal state X_6 and X_5 showing strong absorption, those from X_4 medium absorption, those from X_2 only faint absorption and those from X_1 no absorption. A new table containing some changes and additions is given, using a different notation, which includes nearly all the arc lines. While the numerical relationships of the energy diagram are now well known, the nature of the terms involved has not yet been determined.

ALTHOUGH the number of lines in the tin arc spectrum is not large, the study of the spectrum from the series viewpoint has made very slow progress. A large percentage of the arc lines are readily reversed (especially with a current of 25 amperes) but their distribution is apparently irregular. One cannot by inspection recognize triplets or doublets. It frequently happens that the absorption spectrum of the vapor of an element furnishes a valuable clue to the relationships between the lines. Grotrian[1] has found four lines to be absorbed by tin vapor. McLennan, Young and McLay[2] have extended this number to 16.

The present experiments were undertaken using the methods that were employed in the study of manganese vapor.[3] Between 6000A and 2000A, 53 absorption lines were observed. If the absorption spectrum is photographed with the vapor at the highest temperature (about 1600°C), the intensities of the absorption lines fall quite naturally into three classes, very faint (*f*), medium (*m*) and the strongest absorption lines (*S*). One would expect that the strong absorption lines are due to atoms in the normal state while the very faint lines indicate atoms in excited states.

Table I contains the wave-lengths of all the known lines of the arc spectrum of tin below 6000A together with their frequencies. From

[1] W. Grotrian, Zeits. f. Physik **18**, 169 (1923).
[2] McLennan, Young and McLay, Trans. Roy. Soc. Can. Sec. III, 57 (1924).
[3] Zumstein, Phys. Rev. **26**, 765 (1925).

6000 to 2190A Arnolds'[4] values of the wave-lengths are used. The intensities are as given by Kayser and Runge. Between 2190 and 1950A, the wave-lengths are my own values. The intensities are rough visual estimates of the spectrum of a 50 ampere arc. The maximum error of my measurements appears to be .1A above 2020A and .2A below 2020A. These values may be compared with the measurements of McLennan, Young and McLay[2] who first called attention to the important group of tin arc lines in this region. With a few exceptions, the agreement is very good. Two of their lines are resolved into doublets and 12 new lines are added to their list. Below 1950A the wave-lengths are those found by McLennan, Young and McLay as reversals of a tin arc in an

TABLE I

Tin arc spectrum

λ(I.A.)	ν(I.vac.)	Int. Arc	Int. Abs.	Origin
5631.69	17751.7	5	—	V
4524.740	22094.54	5	—	V
11.30	22160.4	2	—	—
4077.73	24516.5	1	—	—
3801.031	26301.21	4R	f	IV
3655.78	27345.5	3	—	V
3330.596	30016.04	6	*f*	IV
3262.338	30644.06	5R	*f*	IV
23.574	31012.54	1	—	—
18.690	31059.60	3	—	V
3175.039	31486.61	5R	*S*	III
41.823	31819.47	3	—	V
3067.76	32587.62	2	—	—
34.116	32948.96	6R	*S*	—
32.783	32963.45	3R	—	V
09.138	33222.46	6R	*S*	II
2913.542	34312.47	4R	—	V
2863.320	34914.29	6R	*S*	I
50.618	35069.84	4R	*f*	IV
39.985	35201.13	8R	*S*	III
13.582	35531.08	3R	*f*	IV
12.566	35544.28	3	—	V
2790.187	35829.35	2	—	—
89.323	35840.45	1	—	—
87.936	35858.26	4R	—	V
85.027	35896.15	3R	*f*	IV
79.814	35963.03	4R	*f*	IV
61.784	36197.82	4	—	—
06.504	36937.10	7R	*S*	II
2661.245	37565.23	4R	*S*	II
36.988	37910.76	3u	—	V
32.6	37974.		—	V
23.5	38105.		—	V
21.7	38132.		—	V
20.6	38148.		—	—
14.177	38241.55	1	—	—
2599.4	38459.		—	V
94.431	38532.59	4R	*f*	IV
71.598	38874.70	5R	*f*	IV

[4] Arnolds, Zeits. f. wiss. Photographie 13, 322 (1914).

TABLE I—continued

λ(I.A.)	ν(I.vac.)	Int. Arc	Int. Abs.	Origin
58.056	39080.47	4r	—	V
46.552	39257.00	5R	*S*	I
31.122	39496.31	4r	—	V
23.912	39609.13	3R	*f*	IV
10.9	39815.		—	—
2497.724	40024.39	2	—	V
96.768	40039.70	2	—	—
95.722	40056.50	5R	*f*	IV
91.71	40121.0	2r	—	V
83.389	40255.42	5R	*S*	III
55.250	40716.73	3	*f*	III
2433.473	41081.01	2	—	—
29.490	41148.41	6R	*S*	III
21.690	41280.93	6R	*f*	IV
08.143	41513.13	4R	*f*	IV
2380.742	41990.90	3R	*m*	II
68.217	42212.94	1	—	—
57.88	42398.0	1	—	IV
54.840	42452.73	6R	*S*	II
34.799	42817.09	5R	*S*	II
17.21	43142.1	6R	*f*	IV
2286.65	43718.5	4R	*m*	III
82.222	43803.32	3	—	IV
68.902	44060.53	6R	*S*	III
67.160	44094.37	4R	*f*	IV
51.12	44408.9	4R	*f*	IV
46.02	44509.7	6R	*S*	I
31.68	44795.3	4R	*m*	III
11.0	45214.	2R	—	IV
09.60	45242.9	6R	*m*	III
2199.29	45454.9	6R	*S*	II
94.42	45555.8	5R	*m*	III
71.21	46042.8	3R	—	IV
66.72	46137.4	1R	—	—
51.37	46467.3	3R	*f*	III
48.71	46524.8	3R	*m*	IV
48.44	46530.6	3R	*f*	II
47.81	46544.3	1R	—	IV
41.34	46684.9	2R	—	IV
40.65	46700.0	2R	*f*	III 46779 II (Sporer)
23.61	47074.8	1R	—	IV
21.25	47126.9	2R	*f*	IV
18.51	47187.6	1R	—	IV
13.97	47289.4	3R	*S*	II
00.83	47585.1	4R	*m*	III
2098.77	47631.8	1R	—	IV
96.19	47690.4	4R	*f*	IV
94.20	47735.7	2R	*m*	III
93.77	47745.5	1R	—	—
92.41	47776.5	1R	—	IV
91.58	47795.4	3R	*S*	III
85.60	47933.4	1R	—	IV
84.19	47964.9	1R	—	IV
80.51	48049.7	2R	*f*	IV or III
74.75	48183.0	1R	—	—
72.86	48226.9	6R	*S*	I
68.47	48329.3	4R	*m*	III
63.95	48435.1	2R	*m*	II
61.42	48494.7	1R	*m*	IV
59.56	48538.5	1R	*f*	IV
2058.28	48569.0	2R	—	IV
54.05	48670.1	2R	—	IV
40.85	48983.4	3R	*m*	I

TABLE I—continued

λ(I.A.)	ν(I.vac.)	Int. Arc	Int. Abs.	Origin
40.53	48990.9	3R	*m*	III
28.56	49280.0	1R	—	IV
27.15	49314.3	2R	*f*	II
20.79	49469.4	1R	*f*	II
15.75	49593.3	2R	*f*	III
07.90	49787.2	2R		II
1994.30	50126.6	2R		I
92.67	50167.6	1R		—
91.14	50206.1	2R		III
83.39	50402.5	3R		III
70.75	50726.0	2R		II
59.60	51014.4	1R		I or II
51.54	51224.8	3R		III or I
47.6	51329.0	1R		II
41.81	51482.2	1		I or IV
32.32	51734.4	1R		III
24.50	51945.3	2		II
12.61	52268.1	1		III
λ(I.vac.)				
11.3	52320	R		III
08.8	52389	R		—
1899.63	52641.8	3		—
97.05	52713.4	1		I
91.1	52879	R		III
85.8	53028	R		I
82.7	53115	R		III
81.4	53152	R		III
73.3	53382	R		II
72.2	53413	R		—
71.1	53444	R		II
65.6	53602	R		II
63.1	53674	R		III
61.3	53726	R		III
60.3	53755	R		III
54.2	53932	R		II
52.0	53996	R		II
48.5	54098	R		—
37.4	54425	R		III
29.1	54672	R		III
23.1	54852	R		II
19.3	54966	R		III
15.6	55078	R		I
13.0	55157	R		I
08.8	55285	R		I
1804.6	55414	R		II
03.2	55457	R		II
1795.7	55688	R		I
92.0	55803	R		I
87.4	55947	R		—
80.4	56167	R		II
79.3	56202	R		II
78.0	56243	R		I
73.4	56389	R		I
72.8	56408	R		II
71.4	56452	R		—
66.8	56599	R		—
65.7	56635	R		—
64.8	56664	R		III
63.6	56702	R		II
61.7	56763	R		—
56.1	56944	R		—

atmosphere of hydrogen, and are a very valuable contribution to our knowledge of the tin arc spectrum. Those lines at which I have observed absorption by the vapor are indicated in column 4, Table I by the letters *f*, *m* or *S* which represent the magnitude of the observed absorption.

On the basis of their own experiments and the work of others (see their paper for complete references) McLennan, Young and McLay give a table of frequency differences. Sponer[5] has recently given a similar table. The faint arc lines reported by Sponer are also included in Table I. These two tables of frequency differences have been used to interpret the absorption experiments. Most of the lines of column X_6 (McLennan, etc. notation) show strong absorption supporting their opinion that these lines represent transitions to the normal state. Strong absorption is also observed for the lines which come from the X_5 state. This is not surprising as X_5 is an excited state differing in frequency from the normal state by only 1692 cm^{-1}. The absorption lines from the X_4 state ($X_6-X_4=3428$ cm^{-1}) are in the medium class. From the X_2 state ($X_6-X_2=8324$ cm^{-1}) only faint absorptions were observed and finally from X_1 ($X_6-X_1=16873$ cm^{-1}) no absorptions were observed. In general, therefore, the intensities of the absorption lines support their table of frequency differences.

One naturally wonders if every tin arc line finds a place in this table or if there are more excited states close to the normal state. Several lines occupy two positions in their table. For example, 35544.3 (using frequency rather than wave-length) represents a transition to both the X_1 and X_3 states. The fact that no absorption was observed for this line shows clearly that the transition is to the X_1 state. 48676 is given as a transition to the normal state. It should therefore be absorbed rather strongly by the vapor. No trace of absorption was found. 41081.1 should be a medium absorption line but absorption was not observed. Proceeding in this manner, a new table of frequency differences has been made and is given in Table II. It is based primarily on the two tables already referred to and contains a few changes and several additions as suggested by the absorption experiments and the new arc lines observed. The X_3 state has been omitted as all the ultraviolet lines can be given other places in the table and also because the two red lines 16558.0 and 16845.3 were not observed reversed or absorbed. As regards notation, X_1 is used for the normal state, X_2 for the first excited state etc. From this list we get the last column of Table I. A line of origin IV is one where the transition is to the X_4 metastable state.

[5] H. Sponer, Zeits. f. Physik 32, 24 (1925).

Of the 53 absorption lines observed, 52 fit in Table II and in general with the approriate intensities. A glance at column 5, Table I, shows

TABLE II

Frequency differences—tin arc

X_5V 8549.5	X_4IV 5185.5	X_3III 1735.9	X_2II 1692.	X_1I (Normal state)
17751.7	26301.21	31486.61	33222.46	34914.29
	30016.04	35201.13	36937.10	
22094.54	30644.06		37565.23	39257.00
	35069.84	40255.42	41990.90	
	35531.08	40716.73	42452.73	
27345.5	35896.15		42817.09	44509.7
	35963.03	41148.41		
	38532.59	43718.5	45454.9	
	38874.70	44060.53		
31059.60	39609.13	44795.3	46530.6	48226.9
	40056.50	45252.9		
31819.47		45555.8	47289.4	48983.4
	41280.93	46467.3		
32963.45	41513.13	46700.0	48435.1	50126.6
	42398.0	47585.1	49314.3	(51014.4)
		47735.7	49469.4	
		47795.4		(51224.8)
34312.47		(48049.7)	49787.2	(51482.2)
	43142.1	48329.3		
	43803.32	48990.9	50726.0	
35544.28	44094.37		(51014.4)	52713.4
35858.26	44408.9	49593.3	51329	53028
		50206.1	51945.3	
	45214	50402.5		
	46042.2	(51224.8)		
37910.76			53382	55078
37974	46524.8		53444	
	46544.3	51234.4		55157
38105		51842		
38132	46684.9		53602	55285
38459			53932	
	47074.8	52268.1	53996	55688
	47126.9	52320		
	47187.6			55803
39080.47	47631.8			56243
	47690.4	52879		
	47776.5			56389
	47933.4	53115	54852	
	47964.9	53152		
39496.31	(48049.7)			
	48494.7	53674	55414?	
40024.39	48569.0	53755		
	48538.5	53726	55457?	
40121.0	48670.1			
		54425	56167	
	49280		56202	
		54672	56408	
		54966	56702	
	(51482.2)	56664		

Lines in parentheses occur in two places.

that the lines of the arc spectrum (below λ5600) which do not find a place in the frequency difference list are as a rule the faint emission

lines given only by Arnolds. It seems therefore very probable that some of these do not belong to the tin arc spectrum. Out of 40 lines observed by McLennan, Young and McLay in the Schumann region, only 9 are not classified. We have therefore considerable confidence in Table II and do not consider it probable that there are metastable states between X_1 and X_5. If the value of the X_1 term (59158) as given by McLennan, etc., is correct, then we can calculate the values of all the other terms. The problem of determining the nature of the individual terms is one of considerable difficulty and I have made practically no advance in that direction beyond a few general observations.

The vacant spaces in Table II are largely to be attributed to the selection principle of the inner quantum number. It is also certain that the 5 terms X_1, X_2, X_3, X_4 and X_5 do not at all belong to one system (for example quintet *d*) as there are terms which combine with all 5 and we would have a contradiction to the selection principle for inner quantum numbers. We should expect singlet, triplet, quintet, etc., systems for tin. If there are *p* terms among $X_1, \ldots . X_5$ then by the interval rule the ratios of the separations would be 3/2 for quintets and 2/1 for triplets. We note that $(X_3-X_4)/(X_3-X_1)=3/2$. The very strong absorption line 3034.116 which could not be placed in Table II is one of the strongest absorption lines. It represents a transition to X_1, X_2 or X_3 and may be a combination between a quintet *d* term with inner quantum number 4 and *p* terms of the same system. This would explain the lack of other combinations with the particular term involved. Since we have two systems present it is to be expected that all lines which involve transitions to the X_4 term will be faint absorption lines if both terms are in the same system and may even not be observed as an absorption line if the terms belong to different systems and the dispersion of the spectroscope is not large enough. The lines from the X_1, X_2 and X_3 states while usually observed as strong absorption lines may be faint where we have an intercombination between two systems. In conclusion it may be said that the numerical relationship of the energy diagram for the tin arc spectrum are very well known; the nature of the terms involved, however, is practically unknown.

National Research Fellowship,
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October 31, 1925.

SPACE CHARGE CURRENTS BETWEEN COAXIAL CYLINDERS IN THE PRESENCE OF A GAS

By W. H. McCurdy

Abstract

Approximate theoretical equation for space charge currents between coaxial cylinders with gas present.—Langmuir has derived an equation for the space charge limited current between coaxial cylindrical electrodes in high vacuum. In this paper Compton's equation for the terminal velocity of an ion suffering elastic collisions in an electric field, is applied to the case of space charge currents with gas present. Assuming the pressure sufficient so that the ions reach nearly the terminal velocity and neglecting the contribution of thermal agitation to the velocities of the ions, the following approximate equation is derived: $i=A\sqrt{lV^3}/(aB)^2$, where l is the mean free path, V is the voltage, a is the radius of the outer cylinder, B is a function of the ratio of the two radii (values are given in a table), and A is a constant depending on the charge and mass of the ions.

Introduction

IT is well known that currents carried by ions between any pair of electrodes cannot exceed a definite value which depends on the form of the electrodes and the potential difference between them as well as on the charge and mass of the ions carrying the current. This limit is not in any way dependent on the supply of ions. Langmuir has found that for coaxial cylindrical electrodes in a high vacuum, this limit is given by the equation

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{M}}\frac{V^{3/2}}{r\beta^2} \tag{1}$$

where i is the current per unit length of the electrodes, e and M are the charge and mass of the ions, and β^2 is a function of the ratio of the radii of the outer and inner cylinders.

The present work is an attempt to derive an equation which will give the limiting currents which may be obtained when a gas is present in the space between the electrodes.

Derivation

Compton[1] has found that the terminal velocity which an electron, suffering elastic collisions, will attain in a gas is given by

$$V_t=\tfrac{1}{2}(\Omega+\sqrt{\Omega^2+E^2l^2\ M}/1.134m) \tag{2}$$

[1] Compton, Phys. Rev. **22**, 334 (1923).

where V_t is the velocity in equivalent volts, and Ω is the velocity of thermal agitation, also in volts; E is the electric intensity and m and M the masses of the electrons and gas atoms respectively; l is the mean free path of the electrons.

Similar considerations yield for the terminal velocity of a positive ion, suffering elastic collision,[2]

$$U_t=\tfrac{1}{2}(\Omega+\sqrt{\Omega^2+4.61L^2E^2}) \tag{3}$$

where U_t is the terminal velocity, in equivalent volts, and L is the mean free path of the positive ion. The other symbols have the same significance as before.

Under certain conditions of pressure and electric intensity the velocity of thermal agitation becomes very small compared with the velocity due to the field. This is the case when the electric intensity becomes very large while at the same time the pressure is not so high as to make the mean free path extremely small. Then to a first approximation

$$V_t=\tfrac{1}{2}El\sqrt{M/1.134m} \tag{4}$$

and

$$U_t=\tfrac{1}{2}EL\sqrt{4.61} \tag{5}$$

If u is the velocity of advance of an ion and v_t its random velocity of agitation, it may easily be shown that

$$u=.75Eel/mv_t \tag{6}$$

from consideration of the distance of advance between collisions and of the velocity distribution of the ions.

Poisson's space charge equation for cylindrical coördinates reduces because of symmetry, to the form

$$\frac{d}{dr}\left(r\frac{dV}{dr}\right)=-4\pi\rho r=-2i/u \tag{7}$$

since $i=2\pi r\rho u$, where i is the current per unit length of the electrodes, and ρ is the charge per unit volume of the space.

Substituting for u from (6)

$$\frac{d}{dr}\left(r\frac{dV}{dr}\right)=-\frac{8imv_t}{3eldV/dr}=-\frac{8i}{3}\sqrt{\frac{m}{el}}\sqrt[4]{\frac{M}{1.134m}}\frac{1}{\sqrt{dV/dr}}=A/\sqrt{dV/dr} \tag{8}$$

[2] McCurdy, Phil. Mag. **48**, 899 (1924).

on substituting for V_t from (4) and putting

$$A = -\frac{8i}{3}\sqrt{\frac{m}{el}}\sqrt[4]{\frac{M}{1.134m}} \tag{9}$$

For simplicity, put

$$dV/dr = R$$

Integrating (8) we get

$$-\frac{2}{3}\log\,(A - R^{3/2}) = \log r + c\ . \tag{10}$$

For boundary conditions $r = a$ when $dV/dr = 0$, where a is the radius of the outside cylinder which is the source of the ions.

Then, solving for c and reducing we get

$$R = A^{2/3}\frac{a}{r}\left(1 - \left(\frac{r}{a}\right)^{3/2}\right)^{2/3} \tag{11}$$

Expanding the right side of (11) and substituting back for $R = dV/dr$ we get

$$dV = A^{2/3}\frac{a\,dr}{r}\left\{1 - \frac{2}{3}\left(\frac{r}{a}\right)^{3/2} - \frac{1}{9}\left(\frac{r}{a}\right)^{6/2} - \frac{4}{81}\left(\frac{r}{a}\right)^{9/2} - - - -\right\} \tag{12}$$

Integrating (12)

$$V = A^{2/3}a\left\{\log r - \frac{4}{9}\left(\frac{r}{a}\right)^{3/2} - \frac{1}{27}\left(\frac{r}{a}\right)^{6/2} - \frac{8}{729}\left(\frac{r}{a}\right)^{9/2} - - - -\right\} \tag{13}$$

The boundary conditions here are $r = a$, $V = 0$ and $r = b$, $V = V_0$ where b is the radius of the inner cylinder. The first of these gives the value of the integration constant and substituting for $r = b$ we have (approx.)

$$V_0 = A^{2/3}a\left\{\log\frac{b}{a} + \frac{359}{729} - \frac{4}{9}\left(\frac{b}{a}\right)^{3/2}\right\} \tag{14}$$

to terms in b/a only to the 3/2 power. For a closer approximation this may be carried to higher terms in b/a. If, now, we let

$$B = \left\{\log\frac{b}{a} + \frac{359}{729} - \frac{4}{9}\left(\frac{b}{a}\right)^{3/2}\right\} \tag{15}$$

then

$$V_0 = A^{2/3}aB \tag{16}$$

Putting in the value of A, this reduces to an equation of the form

$$i = -\frac{3}{8}\left(\frac{el}{m}\sqrt{\frac{1.134m}{M}}\right)^{\frac{1}{2}}\frac{V_0^{3/2}}{(aB)^{3/2}} \tag{17}$$

The value of B depends only on the electrodes. The values of B and $B^{3/2}$ are given in Table I for values of the ratio of b/a from 0.500 to 0.005.

Eq. (17) applies to the cases of electron currents. The corresponding equation for positive ions is found to be

$$i = -\frac{3}{8}\left(\frac{eL}{2.15M}\right)^{\frac{1}{2}} \frac{V_0^{3/2}}{(aB)^{3/2}} \tag{18}$$

Discussion

The general case of ionic currents between coaxial cylinders is very complicated and the present analysis is applicable only to a range of gas pressures and fields such that the contribution from thermal agitation to the velocities of the ions may be neglected in comparison with

Table I

Values of (aB) *and* $(aB)^{3/2}$ *calculated for an electrode b of radius* 10^{-3} *cm.* A plot of this function on log paper produces a curve which is straight enough to make interpolation comparatively easy.

$(aB)^{3/2}$ may have the value given, multiplied by either $\pm\sqrt{-1}$. For electrons the factor must be considered as $+\sqrt{-1}$ while for + ions the value of $(V_0/aB)^{3/2}$ must be negative in order that the sign of the current may be correct. When V_0 is considered as positive, the observed current is negative. $\sqrt{-1}$ appears in both numerator and denominator of Eq. (18), since e is negative for electrons, and thus cancels. For positive ion currents e is positive but V_0 must be negative and aB is also negative so no imaginary occurs, but the negative sign must be taken as here the current is positive.

b/a	$-B$	$-(aB)$	$(-aB)^{3/2}$
.50	.358	$.0716(10)^{-1}$	$.608(10)^{-3}$
.45	.440	.0980	.975
.40	.536	.1340	1.550
.35	.658	.1870	2.56
.30	.784	.2615	3.98
.25	.949	.3790	7.36
.20	1.155	.576	13.80
.15	1.429	.951	29.40
.10	1.822	1.822	78.10
.09	1.930	2.145	99.50
.08	2.043	2.660	137.0
.07	2.166	3.10	173
.06	2.323	3.88	242
.05	2.498	4.98	355
.04	2.728	6.80	563
.03	3.013	10.05	1002
.02	3.418	17.10	1308
.01	4.108	41.08	8350
.005	4.828	96.60	29700

the velocities due to the field and such that the ion velocity has approximately the terminal value determined by momentum gain between collisions and loss at collisions. This latter condition implies numerous collisions in the space charge sheath. Most of the work of Langmuir

and Mott-Smith with exploring electrodes has been performed under conditions in which the use of Eq. (1) is justified. In some recent work at Princeton on the low voltage tube discharge, however, conditions were more nearly those postulated in the present analysis, which may be considered as the limiting case opposite to that treated by Langmuir.

An exact examination of the pressure and field conditions under which the present analysis may be expected to hold is extremely difficult. Rigorously it would hold only at infinite pressures and field strengths. This being the ideal condition, we wish to find at what

TABLE II

The distance in which a given fraction of the terminal energy is attained by the ions in the field. Ψ is the fraction of the terminal velocity considered $d\bar{H}_e$, $d\bar{H}$, $d\bar{H}_g$, are the distances in which the electrons attain this fraction of their terminal velocity. $d_{He}{}^+$ $d_H{}^+$, and $d_{Hg}{}^+$ are the corresponding distances for the positive ions of the gases indicated by the subscripts. p is the pressure of the gas in mm.

p (mm)	Ψ	$\bar{d}_{He}$ (cm)	$\bar{d}_H$ (cm)	$\bar{d}_{Hg}$ (cm)	$\overset{+}{d}_{He}$ (cm)	$\overset{+}{d}_H$ (cm)	$\overset{+}{d}_{Hg}$ (cm)
1.0	.5	2.90	1.30	1.96	3.36×10^{-3}	1.76×10^{-3}	2.83×10^{-3}
2.0		1.45	.655	1.05	1.68	.88	1.41
3.0		.965	.430	.65	1.12	.58	.94
5.0		.573	.262	.392	.67	.35	.56
10.0		.290	.131	.196	.34	.18	.28
100.0		.029	.013	.0196	.034	.018	.028
1.0	.7	4.55	2.06	3.33	5.27	2.76	4.43
2.0		2.27	1.03	1.66	2.63	1.38	2.22
3.0		1.52	.68	1.11	1.76	.92	1.47
5.0		.91	.41	.66	1.05	.55	.89
10.0		.46	.21	.33	.527	.276	.443
100.0		.046	.021	.033	.053	.028	.044
1.0	.9	7.75	3.50	5.65	9.0	4.70	7.55
2.0		3.87	1.75	2.83	4.5	2.35	3.77
3.0		2.58	1.17	1.88	3.0	1.57	2.52
5.0		1.55	.70	1.13	1.8	.94	1.51
10.0		.78	.35	.57	.90	.47	.76
100.0		.078	.035	.057	.09	.047	.076

pressures the desired conditions are approximately satisfied. In order to make this possible Table II has been prepared which gives the distances in which the ions attain a given fraction of their terminal velocity. If the calculation shows that the distance in which the ions have attained say 0.9 of their terminal velocity is small compared to the distance between the electrodes, we may be sure that the equations will give at least approximate results. This appears to be the only method of determining the conditions of applicability of the above equations.

The evaluation of the constant of integration in Eq. (10) may seem to be incorrect; for since it is assumed that the velocity of the ions is proportional to the square root of the electric intensity, on substitution of a zero value for this at the outside electrode, we assume a zero value for the initial velocity of the ions, and thus the current must be zero, which is impossible. Since, however, the ions must have a velocity of thermal agitation they will diffuse into the space inside the outer electrode and there be caught by the electric field, while at the same time the velocity of agitation may be so small that it soon becomes insignificant in comparison with the velocity they obtain from the electric field. This means, of course, that the analysis cannot apply rigorously at the outer electrode. The effect of initial velocities on the motion of the ions in such cases as this has been recently considered by Langmuir and Mott-Smith.[3] Consideration of the initial velocities in the present analysis, owing to the limited range over which it is applicable, appears unnecessary. The general conclusion is that Eq. (18) may be used as an approximation provided collisions are sufficiently numerous in the gas between the electrodes to give the ions their terminal speeds quickly.

Though this derivation cannot be considered as rigorous and general, still it seems to give an advance in the direction of determining the effect of collisions on currents between cylindrical electrodes limited by space charge.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.
October 5, 1925.

[3] Langmuir and Mott-Smith, G. E. Rev. **27**, pp. 449, 538, 616, 762 and 810 (1924).

LOW VOLTAGE DISCHARGES IN HELIUM

By W. H. McCurdy and P. Dalton

Abstract

Discharge through helium, .01 to 2.9 mm pressure.—A hot filament cathode and disk anode were mounted in a glass frame 10 to 12 cm apart, the frame being so arranged that it could be moved magnetically inside a glass tube of diameter about 4 cm, with reference to a fixed exploring electrode. Measurements of *potential distribution and of mean energy and concentration of electrons* were made at three pressures, .095, 0.5 and 2.9 mm. Although precautions were taken to secure pure He, striations were obtained because of a trace of neon. The results are similar to those obtained by Bramley for hydrogen.[1] The mean electron energy decreases to a minimum beyond the negative glow, then rises to a maximum beyond the face of the first striation. The electron concentration falls from a maximum in the negative glow to a minimum near the cathode side of the first striation; within the limits of accuracy of the work, it increases in a given region of the discharge with an increase of pressure and is proportional to the current density of the discharge at a given pressure. Calculations of the *positive ion concentrations* by Langmuir's formula and also by one developed by McCurdy, give results which seem to be equal to the electron concentrations, but as both methods are merely approximations, this result is not very reliable.

Introduction

An investigation of the striated discharge in mercury vapor was reported by one of us,[2] but it was found that conditions were satisfactory for only approximate results. It was decided therefore to use helium instead of mercury vapor in order to secure more stable conditions without loss in the advantages to be derived from the use of a monatomic gas. It was found that helium served very well for the purpose of the work.

In the work referred to above the three following equations were used and the derivation of them indicated. Reference to the previous work may be made to secure information concerning these.

$$I = Ne\left(\frac{e\overline{V}}{3\pi m}\right)^{\frac{1}{2}} \epsilon^{-3V/2\overline{V}} \tag{1}$$

$$\overline{V}_{-} = \frac{3}{2\tan\theta} \tag{2}$$

$$I_0 = Ne\left(\frac{e\overline{V}}{3\pi m}\right)^{\frac{1}{2}} \tag{3}$$

[1] Bramley, Phys. Rev. **26**, (Dec. 1925).
[2] McCurdy, Phil. Mag. **48**, pp. 898-917 (1924).

In these I is the current per unit area of the exploring electrode and I_0 is the same when the exploring electrode is at the potential of the surrounding gas; V is the negative potential of the electrode with respect to the surrounding gas, and $\overline{V}_-$ the average velocity of the ions in equivalent volts; N the number of ions per cc of gas; tan θ is $d(\log_e I)/dV$ of the $\log_e I$ *vs* V curves.

These equations permit the determination of the potential at any point in the field and of the concentration and average energy of the electrons, as indicated in the previous work.

In order to study positive ions, we must use a different method. Following Langmuir's[3] theory of space charge sheaths we are able, on making certain assumptions, to determine concentrations of positive ions. If the mean free path of the positive ion is large compared with the thickness of the space charge sheath, we may use Langmuir's[4] space charge equation,

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\,\frac{V^{3/2}}{r\beta^2}$$

where i is the current per unit length of the electrode and V the potential difference between the outside of the sheath and the exploring electrode, and thus determine the ratio of the radii of the outside of the sheath and the exploring electrode. Thus we have a method of calculating the radius of the sheath or the effective collecting area of the exploring electrode for positive ions.

When the ions make numerous collisions while traversing the space charge sheath, the above equation cannot be expected to hold. As this was the case in the most of the present work, an equation was used, which was developed to satisfy such conditions.[5] This equation evaluated for helium positive ions, is

$$i=3.14\times10^{-7}\sqrt{L}\,\frac{V^{3/2}}{(aB)^{3/2}}$$

where i is the current per unit length of the electrode, L the mean free path of the positive ions and (aB) a function of the ratio of the radii of the sheath and exploring electrode. Both methods have been used in making the calculations and both results are given. Examination of the tables will show that, since in most cases the sheath thickness is large compared to the mean free path of the ions, the results obtained by use of the latter equation should be more reliable.

[3] Langmuir, G. E. Rev. **26**, 731 (1923).
[4] Langmuir and K. Blodgett, Phys. Rev. **22**, 347 (1923).
[5] McCurdy, preceding paper in this issue.

In order to calculate the concentration of positive ions at any point in the discharge, we may now use Eq. (3) with appropriate values substituted for the charge and mass of the positive ions involved. This, of course, assumes a Maxwellian velocity distribution, which would be expected to correspond to the actual distribution, at least approximately. A more questionable factor is introduced in determining the average energy of the positive ions. In cases of weak electric fields, it is assumed that the velocity was that of thermal agitation of the gas molecules at the temperature of the gas, which was assumed to be 100°C. For cases of greater field strength, the terminal energy was calculated from the equation derived by one of us for positive ions.[6]

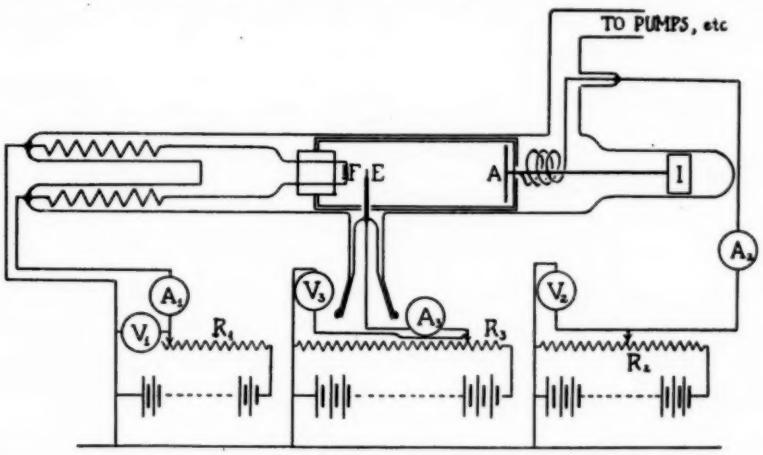

Fig. 1. *F* is the hot tungsten filament cathode, *A* is the anode and *E* the exploring electrode. $A_1 A_2 A_3$ are ammeters in different circuits and $V_1 V_2 V_3$ the corresponding voltmeters, $R_1 R_2 R_3$ are resistances or resistance potentiometers.

Apparatus and Procedure

The experimental arrangement is shown in Fig. 1. The method used was that first developed by Langmuir[7] and used by him in a study of the discharge in mercury vapor. The anode and cathode were mounted in a light glass frame which could be fitted inside a glass tube about 4 cm in diameter. The distance between anode and cathode could easily be varied and the distances used ranged from 10 to 12 cm. The whole could be moved inside the discharge tube by means of an electromagnet and the iron cylinder *I*, thus making it possible to explore any desired part of the discharge by means of the fixed electrode. The electrical arrangements need no explanation.

[6] McCurdy, Phil. Mag. **48**, p. 898 (1924).
[7] Langmuir, G. E. Rev. **26**, 731 (1923).

The helium was purified, before being introduced into the experimental tube, by passing it over a mixture of copper and copper oxide heated to a dull red heat, then through cocoanut charcoal immersed in liquid air. Mercury vapor and stop-cock grease were kept from the system by means of liquid air traps into one of which some gold foil was introduced as an additional precaution against mercury vapor. The tube was carefully baked out before use by heating to about 350°C with good vacuum.

In perfectly pure monatomic gases the positive column is uniform. In spite of the above precautions, a trace of a striation was found at the cathode side of the positive column. This was assumed to be due to a trace of neon present in the helium, which could not be removed by the purification process employed. Spectroscopic evidence for this was found in a separate experiment, in which even more care was taken to remove all traces of impurity from the helium. The system, which included the purifying traps and discharge tube, could be cut off from the evacuation system by means of a mercury cut-off and was protected by liquid air traps. The whole was baked out to a temperature of 500°C under high vacuum and the copper-copper oxide mixture heated to a bright red heat. The metal anode was heated by means of an induction furnace until there was no glow produced by the furnace when the anode was at a very bright heat. The helium was then introduced after preliminary purification and the discharge started, which should cause the helium to flow through the hot copper-copper oxide mixture and through the charcoal in liquid air. Even after continued operation it was found that a trace of a striation still remained at the cathode end of the positive column. The only impurity that could be found spectroscopically was neon which showed very faintly. Thus it seems logical to assume that the neon was the cause of the striation observed. It may also be noted that this agrees with the theory advanced to explain striations in the positive column of the discharge,[8] since several of the critical potentials of neon, including the ionizing potential, are below the lowest radiating potential of helium.

RESULTS

Tables of the average energy of the electrons and concentrations of the electrons and positive ions under different conditions are shown in Tables I, II, III and IV in which the symbols have the following significance: $\overline{V}$ is the average energy of the electrons, N_- is the con-

[8] Compton, Turner and McCurdy, Phys. Rev. **24**, 597-615 (1924) also McCurdy, loc. cit.[3]

centration and I_- the electron current per unit area of the exploring electrode; I_+ is the positive ion current per unit length of the exploring electrode, a_1 and a_2 are the radii of the outside of the sheath as calculated by Langmuir's and the author's equation respectively, N_1^+ and N_2^+ are the positive ion concentrations as calculated from the corresponding radii.

TABLE I

Results for helium at 2.9 mm pressure. Length of the discharge 11.6 cm. $\overline{V}_+$ assumed to be .049 volts in values marked*, otherwise $\overline{V}_+$ was calculated to be .110 volts. Tube current 90 m.amps. D is the distance from the anode.

D (cm)	I_- ($\times 10^2$)	$\overline{V}_-$ (volts)	N_- ($\times 10^{-9}$)	I_+ ($\times 10^3$)	a_1 ($\times 10^2$)	a_2 ($\times 10^2$)	N_1^+ ($\times 10^{-9}$)	N_2^+ ($\times 10^{-9}$)
Cathode								
11.35	252.	3.6	293.	1.75	1.57	2.11	*312.	*232.
11.0	197.	2.02	336.	1.12	1.86	2.56	*168.	*122.
10.5	79.	2.02	123.	.526	2.20	3.70	*57.	*40.0
10.0	27.8	2.22	42.	.253	3.0	5.25	*23.6	*13.5
9.0	5.91	2.46	16.5	.098	4.8	9.90	*5.7	*2.17
7.5	3.95	6.55	7.4	.112	4.9	10.6	4.27	2.02
1st Striation								
6.9	3.15	6.9	5.3	.161	4.6	10.1	6.55	2.9
6.3	3.15	8.0	4.5	.234	4.25	8.5	10.3	5.15
5.1	3.55	6.9	6.4	.365	3.68	7.05	18.5	9.60
2nd Striation								
4.4	3.79	8.35	12.2	.356	3.82	7.52	17.4	8.80
3.7	.52	6.0	9.3	.263	4.62	9.35	10.6	5.27
Anode								

TABLE II

Results for helium at .5 mm pressure. Length of the discharge 12.0 cm. $\overline{V}_+$ assumed to be .049 volts in values marked*, otherwise $\overline{V}_+$ was calculated to be .430 volts. Tube current 50 m.amps. D is the distance from the anode.

D (cm)	I_- ($\times 10$)	$\overline{V}_-$ (volts)	N_- ($\times 10^{-9}$)	I_+ ($\times 10^3$)	a_1 ($\times 10^2$)	a_2 ($\times 10^2$)	N_1^+ ($\times 10^{-9}$)	N_2^+ ($\times 10^{-9}$)
Cathode								
11.9	.92	3.26	22.2	.795	5.06	7.89	*44.1	*27.9
11.7	1.58	3.0	40.2	.558	5.75	9.15	*27.6	*17.4
11.3	1.24	2.14	37.5	.460	6.10	10.0	*21.1	*12.8
10.7	.84	1.95	26.5	.348	6.58	11.3	*14.3	* 8.3
10.1	.48	1.82	15.7	.208	8.95	16.1	* 6.52	* 6.8
9.3	.26	2.14	17.9	.130	11.35	18.8	* 3.21	* 1.95
8.3	.14	3.28	3.43	.124	11.75	19.4	* 2.95	* 1.87
7.3	.156	4.95	3.13	.171	9.70	16.0	* 4.95	* 2.99
1st Striation								
6.3	.072	6.51	1.24	.208	10.20	16.6	1.93	1.19
5.3	.132	8.7	1.98	.192	10.50	17.7	1.74	1.05
4.3	.120	9.15	1.75	.171	11.25	18.8	1.43	.86
3.3	.088	7.85	1.39	.166	11.50	19.2	1.36	.82
2.3	.080	8.5	1.21	.179	11.90	20.2	1.42	.84
2nd Striation								
1.3	.072	7.05	1.20	.166	12.20	20.9	1.29	.75
Anode								

TABLE III

Results for helium at .095 mm pressure. Length of discharge 10 cm $\bar{V}_+$ assumed to be .049 volts for all computations as the electric intensity is very small at all points given in the table. In this case, the positive column has not appeared in the region explored. Only the negative glow and cathode end of the Faraday dark space are present. Tube current 50 m.amps.

D (cm)	I_- ($\times 10^2$)	$\bar{V}$ (volts)	N_- ($\times 10^{-9}$)	I_+ ($\times 10^3$)	a_1 ($\times 10^2$)	a_2 ($\times 10^3$)	N_1^+ ($\times 10^{-9}$)	N_2^+ ($\times 10^{-9}$)
9.95				.195	21.5	31.8	2.55	1.72
9.9				.332	19.3	29.4	3.38	2.21
9.8				.312	15.9	27.4	5.52	3.19
9.6				.348	14.6	26.3	6.65	3.70
9.2	1.57	8.1	2.54	.296	13.0	24.3	6.40	3.41
8.4	2.16	7.85	3.40	.267	14.3	25.6	5.23	2.92
7.2	1.60	7.3	2.62	.238	15.2	26.2	5.38	2.51
6.0	1.68	7.85	2.64	.224	16.6	27.7	3.78	2.26
5.0	1.28	7.3	2.09	.251	15.4	26.8	4.39	2.62
4.0	1.08	7.6	1.73	.256	15.0	26.3	4.62	2.73
3.0	.50	7.85	.79	.243	15.7	27.4	4.41	2.48
2.0	.44	6.8	.74	.232	15.7	27.6	4.18	2.35
1.0	.28	7.05	.47	.229	15.3	26.8	3.98	2.38
.4	.26	7.2	.43	.195	16.7	27.9	3.25	1.96

TABLE IV

Comparison of the concentration of electrons with the current density of the discharge. Pressure was 2.9 mm., voltage across the tube was 83 volts and the length of the discharge 11.6 cm. D is the distance of the point from the anode in cm. N_{90}^- is the concentration with a discharge current of 90 m.amps. N_{180}^- is the concentration with a discharge current of 180 m.amps.

D	N_{90}^-	N_{180}^-
anode		
3.5 cm	7.6×10^9	16.8×10^9
5.0	7.6	14.8
6.0	4.7	11.4
7.0	5.6	11.6
9.0	16.5	26.0
10.0	42	90
10.5	123	280
11.0	336	660
11.3	300	520
cathode		

1. *Potential distribution.* Owing to the striation of the positive column, it was found that the potential gradient in the positive column was not uniform, but resembled in general that found in earlier work on mercury by one of us, and in hydrogen in recent work by Bramley.[9] The continuous curves in Figs. 2 and 3 show the potential distribution at two different pressures, 2.9 and 0.5 mm respectively.

[9] Bramley, Phys. Rev. **26**, (Dec. 1925).

In the negative glow the potential gradient is very small or zero at higher pressures and is negative at lower pressures. The field gradually increases from the negative glow through the Faraday dark space to

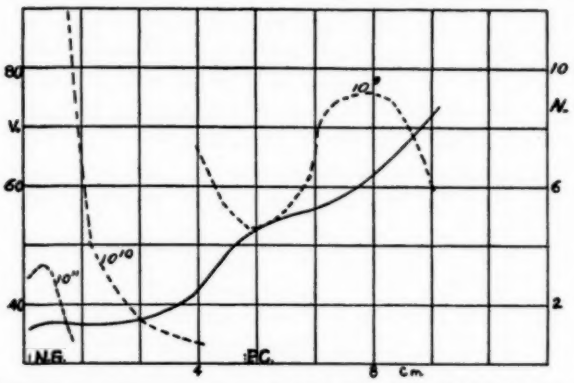

Fig. 2. Full curve represents potential distribution with ordinate given on left. Broken curve applies to electron concentration with ordinates given on the right multiplied by factors entered above each section of curve. Pressure 2.9 mm.

the positive column, reaches a maximum about the head of the positive column and falls off again inside the positive column. This also is in agreement with Bramley's results on hydrogen and the less conclusive

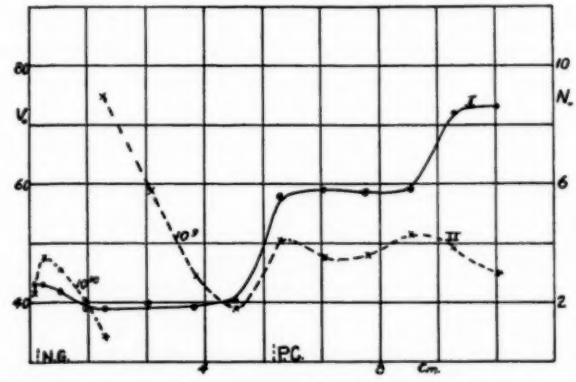

Fig. 3. Full curve represents potential distribution with ordinate given on left. Broken curve applies to electron concentration with ordinates given on the right multiplied by factors entered above each section of curve. Beginning of the negative glow is about N.G. and the positive column about P.C. Press. 0.5 mm.

results on mercury already referred to, and also with results on low voltage arcs in argon reported by Compton and Ekart.[10] This negative gradient is necessary in order to account for the observed currents in the discharge.

[10] Compton and Ekart, Phys. Rev. **24**, 97 (1924).

2. *Average energy of electrons.* The average energy of the electrons was calculated from the $\log_e I$ *vs* V curves by Eq. (2). It was found that the average energy of the electrons was independent of the current density of the discharge but depended on the pressure of the helium. This was to be expected as it was found that the potential distribution was little affected by current strength and thus the average energy of electrons should also be independent of the current strength. Comparison between tables I, II and III shows that, at corresponding points of the discharge the average energy of the electrons increases with a decrease of pressure, except at points in the negative glow, in which case the increase in the current with the voltage in the curves from which the average energy is calculated is so rapid as to render accurate determinations of the average energy very difficult. It may therefore be stated that the average energy of the electrons in a given region of the discharge increases with a decrease of pressure. This is what should be expected from Compton's[11] equation for terminal velocities of electrons in a gas. Sufficiently accurate data have not been obtained however, to make numerical comparisons with Compton's equation.

3. *Electron Concentration.* The variation of the electron concentration with different factors in the discharge is closely related to the variation of the electron energy. Since the average energy has been found to be independent of current density in the discharge, the electron concentration should be proportional to the current carried by the discharge. By making determinations of the concentrations of the electrons at different currents, other conditions remaining constant, it was found that within the limts of accuracy of the experiments the concentration of the electrons was proportional to the current density of the discharge current. Results of this work are given in Table IV. Further, since the average energy was found to increase with a decrease of pressure, the concentration of electrons, necessary to produce a given current, should decrease with a decrease of pressure. Results given in Tables I, II and III appear to indicate that this is actually the case. As in the case of average energies, however, the experimental data are not sufficient, either in volume or accuracy, to enable a relation between pressure and concentration to be determined.

The mechanism of conduction, at best, must be complicated, since in all parts of the discharge we must have present in varying degrees both conduction and diffusion currents which together produce the observed discharge currents. Consequently a prediction as to how any

[11] Compton, Phys. Rev. **22**, 334 (1923).

factor should depend on any other must be based on very elaborate experimental data.

4. *Positive ion concentration.* It will be noted from the tables that the positive ion concentration has in all cases been calculated by the use of two different equations. In all cases but the last it may safely be assumed that Langmuir's space charge Eq. (4) cannot be expected to give accurate results as, on the average, the positive ions must suffer several collisions inside the space charge sheath. Further, Eq. (5) would appear to give a more reliable result, except possibly in the negative glow where the sheath thickness is not very large compared with the distance in which the positive ions attain .9 of their terminal energy, since the conditions of derivation of this equation are more nearly fulfilled than those underlying Langmuir's equation. The average electric intensity within the sheath is in all cases much greater than 100 volts per cm which would make the velocity of thermal agitation very small compared to that produced by the action of the electric field on the ion. Thus the values given under N_2 in tables I and II appear more reliable, while those under N_1 are probably more reliable in Table III.

In all cases the concentration of positive ions is very large in the negative glow and falls off towards the positive column. Inside the striations it has a varying value which follows closely the variations of the electron concentration. Also in the majority of cases the agreement in actual values between the electron and positive ion concentrations is fair. There is in no part of the discharge a great preponderance of ions of either sign, which must be true since the potential distribution shows no effect of large space charge at any point of the discharge, except within the cathode drop, which we could not explore by this method on account of its very small thickness.

Any data concerning positive ions must, at best, be only rough approximations. We have at present no method of determining directly the energy of the positive ions under the conditions which are maintained in the discharge and thus an error of 100 percent or more may occur. Thus the agreement found in this work appears satisfactory.

Conclusion

The results here reported appear to confirm, in some respects at least, the theory advanced by Compton, Turner and McCurdy,[8] in that the concentration gradient of electrons[12] is sufficient to account

[12] For a discussion of the necessary negative potential gradient in the negative glow reference must be made to the papers referred to above.[8] It is there pointed out that a

for the current in the negative glow and Faraday dark space. The negative potential gradient in the negative glow is found to occur at low pressures while at higher pressures the gradient is very small or zero. The observed negative gradients are of the order demanded by the kinetic theory of ionic diffusion. Also the cathode side of the striations appears to be a region of ionization and of positive space charge.

Sufficient data were not obtained to enable any numerical relations between average energy and concentration of electrons and the gas pressure to be established.

In conclusion, the authors wish to express their most sincere thanks to Professor K. T. Compton for his interest in the work, and valuable suggestions throughout the course of the investigation.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.
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negative gradient in this region is necessary, since the current produced by the diffusion of electrons as calculated on the basis of the kinetic theory is larger than the observed current, thus a negative electron current is necessary to explain the observed facts.

THE UNIVERSAL CONSTANT OF THERMIONIC EMISSION

By P. W. Bridgman

Abstract

Theoretical deduction of the formula for thermionic emission.—The constant A of the thermionic emission formula: $I = AT^2e^{-b_0/T}$ has been shown by Richardson and Dushman by different lines of argument to be a universal constant, and a value for the constant has been deduced by Dushman. The experimental data of Dushman verify this value of A for pure metals, but if the metal is coated there are very wide divergences. In this paper an attempt is made to give a more rigorous deduction of the emission formula, so that it may be plain under what conditions it may be expected that A be universal. Assuming that the entropy of the electron gas is the same as that of an ordinary monatomic gas in the Sackur Tetrode theory, and also assuming that the entropy of a surface charge is zero at 0° Abs. it is shown that an emission formula of the type above necessarily demands that A have the universal value assigned by Dushman, and the necessary and sufficient condition for this is that the difference between the specific heat of the neutral metal and of a charge on its surface vanish ($C_{pm} - C_{pp} = 0$). This condition may also be formulated in terms of the surface heat and is equivalent to $\sigma + dP_s/dT - P_s/T = 0$, where P_s is the surface heat and σ the Thomson heat. If σ can be neglected, the emission formula holds with the form given when P_s is proportional to absolute temperature.

Physically it seems probable that (1) if the metal is uncoated the forces on the surface ions are nearly the same as on the neutral atoms, so that the condition $C_{pm} - C_{pp} = 0$ is satisfied, but (2) if the surface charge has the properties of a gas, as in an oxygen coated filament, (a) the specific heat may be different from that of the metal, or more probably (b) the entropy of the surface charge may not vanish at 0° Abs.; and (3) if the surface is coated with another more easily ionizable metal there may be electrical forces on the surface ions which modify their specific heat.

Introduction

IN two recent papers Dushman[1] has given a theoretical deduction of the constant A of the formula of thermionic emission

$$I = AT^2e^{-b_0/T}$$

and has discussed the agreement with experiment in the light of new and more accurate data. The deduction of the value of A involves the Sackur-Tetrode theory of the entropy constant of a monatomic gas (which here is the electron gas in contact with the metal), and the value found by Dushman is $A = 2\pi k^2 m\epsilon/h^3$.

[1] S. Dushman, Phys. Rev. **21**, 623-636 (1923); **25**, 328-360 (1925).

In a note commenting on the first paper of Dushman, Richardson[2] points out that as early as 1915 he had, by a purely thermodynamic argument not involving quantum theory, shown that A is a universal constant, and had even gone further, and by an argument involving quantum theory, had found the factors $k^2m\epsilon/h^3$ in A, but with a numerical coefficient different from 2π.

Experimentally Dushman found that the formula is entirely satisfactory for tungsten, for which the experimental data are most accurate, and probably is satisfactory for molybdenum and tantalum, for which the data are less accurate, but that if the emitting substance is not a pure metal, but is coated, the values of A range from 5×10^{11} to 3×10^{-3} (1925 paper, page 358). It would appear, therefore, that the arguments of both Dushman and Richardson must neglect some factor which is not important for pure metals, but which may be very important indeed in the more general case to which their arguments apply at least by implication.

Dushman states that his theoretical deduction of A neglects the surface heat, and that the agreement of the formula for tungsten indicates that for this metal the surface heat is small. Dushman, however, does not show at all in detail how the surface heat is concerned in the deduction of the formula, so that although we may be willing to accept his statement that the formula could be obtained by neglecting the surface heat, it is not at all obvious that conversely we may infer that, if the formula holds, the surface heat must be zero. The question of the surface heat was discussed by me at considerable length in the Physical Review[3] several years ago. It is a reversible heat which must be added or subtracted when an electrical charge is applied to or removed from the surface of a conductor isothermally. The possible existence of this surface heat has been neglected in nearly all thermodynamic discussions of this subject.

The original and fundamental thermodynamic discussion of Richardson has been recognized for some time to be lacking in rigor because of his interchangeable use of quantities thermodynamically different. Schottky pointed this out in 1915,[4] and I also discussed the matter at some length[3] (without knowledge of Schottky's work, which was inaccessible because of the war), and gave corrected forms for several of Richardson's formulas. Richardson has recently recognized[5] that

[2] O. W. Richardson, Phys. Rev. **23**, 153-155 (1925).
[3] P. W. Bridgman, Phys. Rev. **14**, 306-347 (1919).
[4] W. Schottky, Verh. D. Phys. Ges. **7**, 109-121 (1915).
[5] O. W. Richardson, Proc. Roy. Soc. **105**, 403 (1924).

he did neglect the difference between two quantities really different, but his present position is that as a matter of experiment the difference is small, and he points to recent experiments on tungsten as justification. He characterizes as "severe" my criticism that "the neglect of the surface heat in Richardson's equation would therefore seem to be indefensible, and until the order of the effect is known we cannot tell whether Richardson's equation is even approximately correct." In view of possible experimental variations from 5×10^{11} to 3×10^{-3} it does not seem to me that this remark is "severe."

It is the purpose of this paper to present a derivation of the thermionic emission equation without the approximations of either Richardson or Dushman, to find under what conditions the formula reduces to the simple form given, and in particular what are the necessary assumptions about the surface heat, and finally to discuss what may be the physical basis for the evident difference between the value of A for coated and uncoated conductors.

Deduction of the Thermionic Emission Formula

It must in the first place be said that it is recognized by everyone that there is an uncertain element in the formula for thermionic emission current in that it is necessary to assume no reflection of electrons on impinging on the metal surface from the gas. Thermodynamically we can find only the density (or pressure) of the electron gas in contact with the metal under equilibrium conditions. To pass from electron density to saturation current involves kinetic theory, assuming Maxwell's distribution of velocity, and also the assumption of no reflection.[6] In the following discussion we consider, instead of the emission current, the electron gas pressure. Under the usual assumptions of kinetic theory Dushman's formula is then equivalent to

$$p=\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}T^{5/2}e^{-b_0/T}$$

where p is the density of the electron gas at points immediately outside the metal, and the significance of the other letters is the conventional one. (I shall assume here as known and accepted the results of

[6] In this discussion no consideration is to be given to the somewhat modified form of the universal constant which would be obtained if the theory of G. N. Lewis of ultimate rational units is accepted. In view of the considerable uncertainty arising from the effect of electron reflections at the surface, I do not believe that any measurements of the saturation current are able at present to distinguish between the two values of the constant.

the long discussion between Schottky and v. Laue as to the justifiability of treating the electron atmosphere as a perfect gas.)

It should also be said that the new ideas about the entropy constant of a monatomic gas were first applied to the electron vapor by v. Laue,[7] who obtained a value for p in which the coefficient of the exponential term is exactly that of Dushman, but which has the exponential term $e^{-\mu/RT}$. Here μ is the so-called "electron affinity" of the electron for the metal. v. Laue explicitly recognized and stated that μ may be a function of temperature. If there are terms in μ proportional to the temperature the universal constant will obviously be modified, and in any event the formula does not reduce to that above unless μ is a constant. Physically, "electron affinity" is a concept most difficult to interpret in terms of quantities directly measurable, so that the formula as given by v. Laue actually becomes an equation for finding "electron affinity" in terms of emission data, and is therefore not adapted to our purposes, although from the thermodynamic point of view no criticism can be made of the rigor of the deduction.

Given now a neutral metal at 0° Abs. We raise it, in the neutral condition, to the temperature T, and at this temperature evaporate from it reversibly at the equilibrium pressure a certain number of electrons, leaving behind on the surface of the metal in the form of surface charge an equal and opposite positive charge. The final system consists of electron vapor, surface charge, and remaining neutral metal. For the purposes of this argument we may imagine that all the neutral metal is evaporated, leaving a final system of only vapor and surface charge. The entropy of the final system is the sum of the entropy of the gas and of the surface charge. If we accept the dictum of the third law that the entropy of the neutral metal is zero at 0° Abs., the entropy of the final system is also equal to the entropy imparted to the neutral metal on warming from 0° Abs. to T plus the entropy change during evaporation. The entropy of the electron gas per electron is

$$s_0+(5/2)k \log T-k \log p$$

where, according to the Sackur-Tetrode theory s_0 has the value:

$$s_0=k\left(5/2+\log\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}\right)$$

The entropy change of the system during evaporation is η/T, where η is the latent heat of evaporation per electron, *the system being isolated so that during the evaporation a compensating surface charge is left on the metal.* The entropy change of the neutral metal during heating is

[7] M. von Laue, Jahrb. d. Rad. u. Elek. **15**, 257-270 (1918).

$\int_0^T (C_{pm}/T)dT$, where C_{pm} is the specific heat at constant pressure of that number of atoms of the neutral metal which give rise to one electron of vapor. The entropy of the surface charge, assuming that the surface charge acts like a condensed system so that its entropy at 0° Abs. vanishes, is $\int_0^T (C_{p\rho}/T)dT$, where $C_{p\rho}$ is the specific heat at constant pressure of the surface charge left when one electron evaporates. Equating these entropies gives

$$\eta/T + \int_0^T (C_{pm}/T)dT = k\left(5/2 + \log \frac{(2\pi m)^{3/2}k^{5/2}}{h^3} + (5/2)\log T - \log p\right) + \int_0^T (C_{p\rho}/T)dT .$$

This equation may be solved for p, giving

$$p = \frac{(2\pi m)^{3/2}k^{5/2}}{h^3} T^{5/2} e^{5/2 - \eta/kT + (1/k)\int_0^T [(C_{p\rho} - C_{pm})/T]dT}.$$

In this expression everything except the exponential is of the form deduced by Dushman. Our immediate problem is then to find under what conditions the exponent reduces to $-b_0/T$. We must in the first place use what information we have about η, which is a function of temperature. One relation is immediately obtained from general thermodynamics. We have for the latent heat of any transition

$$\frac{d\eta}{dT} = \frac{\eta}{T} - \frac{\eta}{\Delta v}\left(\frac{\partial \Delta v}{\partial T}\right)_p + \Delta C_p.$$

Here Δv is the change of volume during the transition, and ΔC_p is the difference between the specific heat of the system before and after the transition. Applied to the electron vapor, we may in the first place neglect the volume of the metal and surface charge compared with the volume of the vapor, putting $\Delta v = v = (kT/p)$. ΔC_p, which for usual systems consist of only two terms, here consists of three terms, arising from the gas, the surface charge, and the neutral metal.

$$\Delta C_p = C_{pg} + C_{p\rho} - C_{pm} .$$

For a monatomic gas $C_{pg} = (5/2)k$. Substituting these values gives

$$\frac{d\eta}{dT} = \Delta C_p = (5/2)k + C_{p\rho} - C_{pm} ,$$

which gives on integrating

$$\eta = \eta_0 + (5/2)kT + \int_0^T (C_{p\rho} - C_{pm})dT .$$

Substituting back in the value for p, we obtain

$$p=\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}T^{5/2}e^{-\eta_0/kT-(1/kT)\int_0^T(C_{p\rho}-C_{pm})dT+(1/k)\int_0^T(1/T)(C_{p\rho}-C_{pm})dT}.$$

Now to find under what conditions the exponent has the desired form, we put

$$-\eta_0/kT-(1/kT)\int_0^T(C_{p\rho}-C_{pm})dT+(1/k)\int_0^T(1/T)(C_{p\rho}-C_{pm})dT=-b_0/T.$$

Differentiate by T, giving

$$\eta_0/kT^2+(1/kT^2)\int_0^T(C_{p\rho}-C_{pm})dT=b_0/T^2.$$

Multiply by T^2 and differentiate again, giving

$$C_{p\rho}-C_{pm}=0.$$

Hence we see that the vanishing of $C_{p\rho}-C_{pm}$ is a necessary and sufficient condition for the formula found by Dushman with his value of the constant. We may go further and inquire under what conditions the formula takes the form $A'T^{5/2}e^{-b_0/T}$ where A' is some constant different from that above. The question is at once answered like that above by putting the exponent equal $-b_0/T+Const.$ Differentiation, as before, again shows that $C_{p\rho}-C_{pm}=0$, so that we conclude that if the expression $A'T^{5/2}e^{-b_0/T}$ holds, both $C_{p\rho}-C_{pm}$ must vanish, and A' must have the universal value above.

The conclusions of the last paragraph have involved the assumption that the surface charge acts like a condensed phase in so far as to have zero entropy at 0° Abs. If this condition is not satisfied, there will be a constant in the exponent, so that there results a formula $A'T^{5/2}e^{-b_0/T}$ with a value for A' different from the universal constant above.

That Dushman has essentially neglected the term $C_{p\rho}-C_{pm}$ may be seen by a detailed examination of his argument, particularly his equation (2) on page 624, and his remarks at the bottom of page 624 and top of page 625.

The conditions under which the general formula with the accepted universal constant is valid have thus far made no mention of the surface heat. The connection may now be shown as follows. Equation (28) of my previous paper,[3] deduced by cyclic operations suggested by Richardson's analysis and entirely different from any used in deducing the previous value of $d\eta/dT$ is equivalent to the equation

$$d\eta/dT=(5/2)k-\epsilon(\sigma+dP_s/dT-P_s/T).$$

Here P_s is the heat which must be absorbed by the system to maintain it isothermal when one unit of electricity is added to the surface, and σ is the Thomson heat as ordinarily defined. Equating the two values of $d\eta/dT$ gives

$$C_{pm}-C_{p\rho}=\epsilon(\sigma+dP_s/dT-P_s/T) .$$

Hence the assumption implicitly contained in the argument of Dushman, and also in that of Richardson as far as its application to the present problem is concerned, is equivalent to setting $\sigma+dP_s/dT-P_s/T$ equal to 0. Now it is generally considered that σ is small compared with other terms in problems of this character, so that if we neglect it the condition reduces to $dP_s/dT-P_s/T=0$, which demands that P_s be proportional to temperature.

It is therefore not necessary that the surface heat vanish in order that the emission formula hold; numerically it may be large or small provided only that it be proportional to temperature.

Physical Significance of the Conditions

Returning now to the condition expressed in the form $C_{pm}-C_{p\rho}=0$, the experimental data obtained by Dushman suggest that the specific heat of the ionized atoms which constitute the surface charge is the same as that of the neutral metal atoms if the metal is pure, but different if the metal is coated. What may we conceive to be the physical reason for this? If the metal is pure the surface charge consists of ionized atoms scattered about in the surface layer of the crystal lattice of the metal, which reaches to the surface without alteration. The analysis of v. Laue has shown that if the electron vapor is to be treated as a perfect gas and the effect of space charge neglected, the electron vapor can occupy a space only a few free paths thick. Under these conditions the distance between the ions in the surface layer is of the same order of magnitude as that between the electrons in the vapor, and since the electrical forces between the electrons in the vapor are negligible under these conditions, it must also be true that in the surface layer the mutual electrical forces between the ions are negligible compared to the forces holding the ions in the crystal lattice. The natural frequency of the surface ions is then approximately the same as that of the surface atoms, and the specific heat is therefore the same.

If, however, the metal is coated, these conditions no longer hold and we may have various sorts of behavior. If the surface coating has approximately the properties of a gas, as in an oxygen coated filament, the surface atoms have the specific heat of a gas atom, which is only

half that of an atom in the solid at high temperatures, but greater at low temperatures. Or, which seems to me much more probable under these conditions, the failure of the formula may be due to the non-vanishing of the entropy of the surface charge at 0^0 Abs. If on the other hand the coating is another metal, particularly if it is one more easily ionized than the underlying metal, the surface charge will consist of ions of the coating metal. If there is any tendency for the coating atoms to bunch themselves on the surface, the ions to which they give rise will be subject to mutual electrical forces which may modify the specific heat.

One is tempted to try for further information about the precise behavior of $C_{pm}-C_{pp}$ in those substances for which the constant of the emission formula has not the universal value above. This, however, is probably not possible with present experimental data. Our argument above has suggested that $AT^2e^{-b_0/T}$ cannot be the correct form of the emission formula under these conditions, but that this form is only an approximation. Before we can reason back to the behavior of the specific heats we must know the correct form of the function. It is presumably impossible to do this with sufficient precision until experimental accuracy is very greatly improved, as is suggested by the fact that until very recently it was impossible to decide whether a formula with T^2 or $T^{\frac{1}{2}}$ fitted better the experimental data.

THE JEFFERSON PHYSICAL LABORATORY,
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November 15, 1925.

THE DIELECTRIC CONSTANT AND MOLECULAR WEIGHT OF BROMINE VAPOR

By Linus Pauling*

Abstract

It is shown that the conclusion reached by Bramley in a recent article that bromine has the formula $(Br_2)_6$ is inconsistent with previous results relating to the density of this substance in the gaseous state and that it is not theoretically justified by the considerations presented by the author.

In a recent paper entitled "Measurements of Velocity of the Synthesis of Hydrogen Bromide by Capacity Change" Arthur Bramley[1] has reported that his experiments lead to a value of 1.0128 (reduced to 0° and 1 atm.) for the dielectric constant of bromine vapor, from which he draws the conclusion that bromine has the formula $(Br_2)_6$. Assuming that bromine vapor consists of diatomic molecules, he calculates from Lorentz's formula $\kappa - 1 = C\rho$, where ρ is the density and C a constant evaluated from measurements on liquid bromine, that the dielectric constant κ should be 1.0022. Furthermore, from the index of refraction n of bromine vapor, 1.00115 (reduced to 0°C. and 1 atm.) and the equation $\kappa = n^2$, he finds a nearly equal value 1.0023. Since his observed value of $\kappa - 1$ is almost six times that calculated for Br_2, he concludes that bromine vapor must have the formula $(Br_2)_6$.

This conclusion is, however, not in accord with density investigations. In an extensive series of vapor-density experiments, E. P. Perman[2] has shown that except at very high temperatures bromine vapor consists entirely of diatomic molecules. Vapor-densities (referred to that of hydrogen as unity) from one series of experiments at 14.7-15° are given in the accompanying table.

Pressure in mm.	98.65	63.70	32.10	16.65
Vapor-density	80.3	80.4	81.3	83.3

Professor Perman concludes "These results show that, on approaching the liquid state, bromine has no tendency to form molecules with more than two atoms. This agrees with the results of Paterno and Nasini[3] by Raoult's method, which indicated molecules Br_2 in aqueous and acetic acid solutions." He further states that experimental errors

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[1] A. Bramley, Phys. Rev. **25**, 858 (1925).

[2] E. P. Perman, Proc. Roy. Soc. **48**, 45 (1890).

[3] Paterno and Nasini, Deutsch. Chem. Ges., Ber. **21**, 2153 (1888).

account for the apparent increase in vapor-density at very low pressures; this increase of course could not be adduced as evidence of the formation of molecules with more than two atoms, for this would contradict the principle of Le Chatelier.

The value reported by Bramley for the dielectric constant of bromine vapor is surprisingly high, in view of the fact that diatomic bromine molecules presumably do not have large electric moments. It is unfortunate that the investigator published none of his experimental data on capacity measurements and determinations of the partial pressure of bromine, which would have permitted checks on his calculations. It seems probable that the value 1.0128 is incorrect because of large experimental errors, for the capacity measurements represented in the graphs were subject to remarkably large fluctuations, amounting, in fact, in some cases to as much as fifty percent of the total change produced by the reaction. The investigator attributed these fluctuations in his measurements to variations in the amounts of bromine vapor present as Br_2 and as $(Br_2)_6$. Since $(Br_2)_6$ is probably not present this explanation is of course unsatisfactory; even if it were present, familiar statistical mechanical considerations indicate that such enormous fluctuations could not be expected to occur in a chemical equilibrium involving such a large number of molecules.[4]

This uncertainty concerning the experimental work throws doubt also on the final conclusion reached by the investigator that the specific photochemical rate for the chemical reaction considered has a negative temperature coefficient.

California Institute of Technology,
Pasadena, California.
November 20, 1925.

[4] That such fluctuations in a chemical equilibrium do not occur is at once evident if one considers their influence for example on the pressure of the system. From Fig. 2 of Bramley's paper it is seen that the measured capacity of the cell had for a period of two minutes a value greater than the equilibrium value by an amount of over 15% of the total change corresponding to the complete combination of hydrogen and bromine to form hydrogen bromide. Since the capacity measurements are made on all the gas between the two plates in his cell, this result requires that if the volume of the gas (about 1 cc) were kept constant, the pressure would show variations due to the postulated fluctuations from the equilibrium state. As there is liquid bromine present the pressure is at least 150 mm; hence the explanation of his observations advanced by Bramley would require that pressure variations greater than 20 mm and lasting more than two minutes occur in this system. This is, however, obviously not possible; we are led to accept the alternative explanation that the variations are due to experimental error.

TEMPERATURE COEFFICIENT OF MAGNETIC PERMEABILITY OF SHEET STEEL

By T. Spooner

Abstract

The samples tested were annealed punched rings of commercial sheet steel such as is used in electrical apparatus, containing 0.9 to 4 percent silicon. Temperature coefficients were determined in the range from −20° to +46°C. As the induction was increased from 2 to 10 kilogausses, the coefficient decreased from +.12% per 1°C to −.021% for 0.9% Si, from +.08% to −.08% for 2.2% Si, and from −.03% to −.18% for 4% Si. Each curve showed a minimum at 10 kilogausses although the maximum permeability normally occurs at 6 to 8 kilogausses. This minimum corresponds to 2 gilberts per cm and is sharper the higher the Si content. These results indicate that the temperature coefficient is more directly related to the induction than to the permeability.

MUCH information is available concerning the relation between temperature and the magnetic properties of ferro-magnetic materials. This is particularly true with reference to permeability. In general, however, these published data deal either with a large range of temperature or with the properties at fairly high temperatures where the thermo-magnetic transformations take place. The available information over small ranges in the region of room temperature is very meager.

Burrows[1] states that permeability at room temperature increases with temperature for low inductions and decreases for high. He also states that the change in induction for 1°C rise in temperature is greatest in the neighborhood of the maximum permeability.

Sanford[2] has given the most complete data of which we have knowledge for the temperature permeability characteristics in this region. Tests were made on samples of cast iron, wrought iron and low-carbon steel for a temperature range from 3° to 88°C and for magnetizing forces up to 200 gilberts per cm. Test results are given for various heat treatments. Some samples showed a positive temperature coefficient of permeability, some a negative and some a change of sign as the induction increased. In one or two cases the sign of the temperature coefficient was changed by heat treatment.

[1] C. W. Burrows, Bull. Bureau of Standards, Vol. **4**, p. 205 (1907).
[2] R. L. Sanford, Bull. Bureau of Standards, Vol. **12**, p. 1-10 (1915).

No one, apparently, has dealt adequately in the room temperature range with the temperature-permeability characteristics of sheet steel such as is used in electrical apparatus. These characteristics are of importance in connection with theories of magnetism and from a practical standpoint in connection with the performance of electrical measuring instruments which use ferro-magnetic material in the magnetic circuit, such as watt-hour-meters.

This paper gives some test results which have been obtained on commercial electrical sheet for a range of temperatures from $-20°C$ to $+46°C$. Because the values of the temperature coefficients in the room temperature range are small and other effects such as incomplete demagnetization may produce as large or larger changes of magnetic permeability than the temperature changes, great care has to be exercised if accurate data are to be obtained.

Test samples. The samples consisted of punched rings $1\frac{3}{4}$ in. (3.44 cm) o.d. and $1\frac{1}{4}$ in. (3.17 cm) i.d., annealed at about 800°C before testing. There were four samples of .9 percent silicon sheet, .0172 in. (.0437 cm) thick, four samples of 2.2 percent silicon sheet, .014 in. (.0356 cm) thick, and three samples of 4 percent silicon sheet .014 in. thick. Each sample consisted of about 110 grams of rings and each was provided with 170 secondary turns and a common primary of 10 turns. Results are also included for a 2.2 percent and a 4 percent silicon sample consisting of rings 3 in. o.d. and 2 in. i.d. which had been tested previously.

Test methods. The samples were placed in a double kerosene bath, the outer part of which was heated by an electrical resistance or cooled by means of CO_2 snow. The magnetic tests were made by a null method using a variable mutual inductometer and fluxmeter. The primary current in the inductometer and the current in the primary of the samples were reversed simultaneously and the mutual inductometer adjusted until the fluxmeter in series with the secondary windings showed no residual deflection. For a given temperature the magnetizing force was adjusted to a definite value, and with the aid of a transfer switch, the corresponding induction was measured successively for each sample. The m.m.f. was then increased and the process repeated. For $B = 10$ kilogausses the induction was kept constant and the current changed. Samples were carefully demagnetized before testing and were put through the cycle many times (100 or more) for each m.m.f. before readings were taken. A change of 0.1 percent in induction could readily be observed, at least for the higher values.

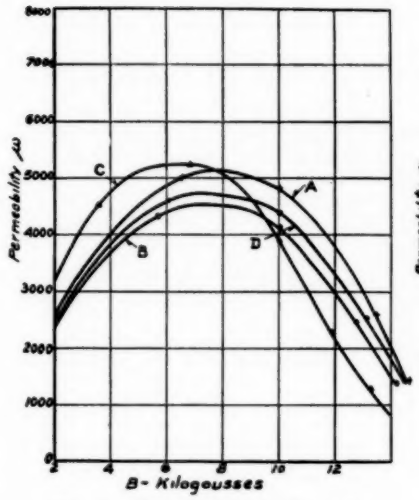

Fig. 1. 0.9% silicon sheet steel. Normal permeability.

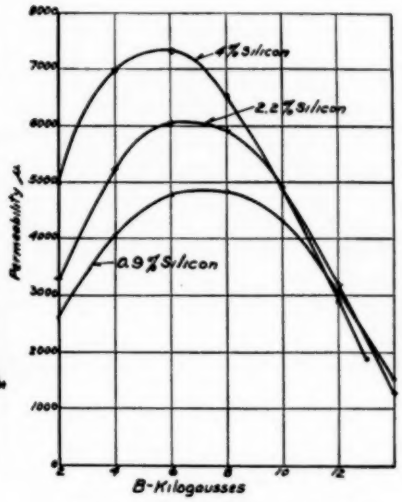

Fig. 2. Electrical sheet steel. Mean permeability.

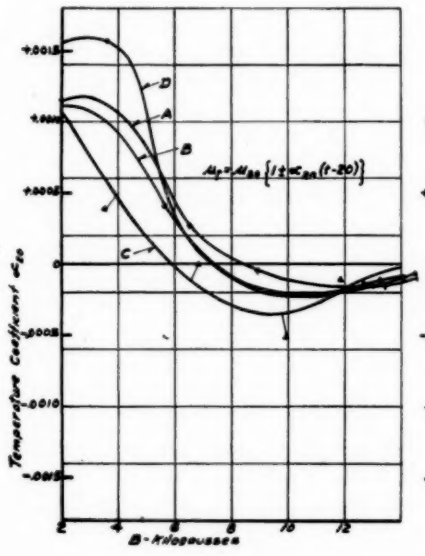

Fig. 3

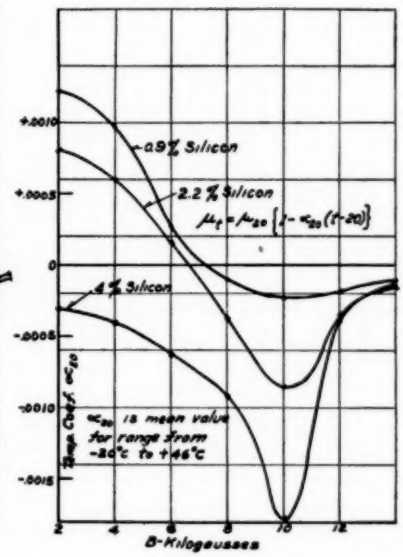

Fig. 4

Fig. 3. 0.9% silicon sheet steel. Temperature coefficient of magnetic permeability as a function of induction, based on the permeability at 20°C.

Fig. 4. Electrical sheet steel. Temperature coefficient of magnetic permeability as a function of induction, based on the permeability at 20°C.

Test results. Fig. 1 shows the permeability values as a function of induction for the four .9 percent silicon steel samples. The letters refer to different samples. Similar curves, not shown, were obtained for the medium and high silicon material.

Fig. 2 shows the average permeability curves for the three classes of material. The medium and high silicon steel curves include the permeability results for the two larger ring samples.

The permeability values for a given sample corresponding to a definite m.m.f. or induction were measured at temperatures of -20, $+1$, $+24.8$ and $+46$°C. The results were plotted against temperature and the best straight line drawn. This assumes that the permeability changes linearly with temperature between -20°C and $+46$°C. Within the accuracy of test this was the case.

The temperature-permeability curves are undoubtedly not straight lines but due to inaccuracies in testing and to the comparatively small temperature range the departures from straight lines are so uncertain that this assumption is probably as reliable as any which could be made from the available data.

From these straight lines the 20° temperature coefficients α_{20} were calculated from the formula,

$$\mu_t = \mu_{20}(1 \pm \alpha_{20}(t-20)) \qquad (1)$$

where μ is the permeability for any temperature t between -20 and $+46$°C, μ_{20} is the 20°C permeability.

Fig. 3 gives the temperature coefficients for the .9 percent silicon steel samples plotted against maximum induction.

Fig. 4 gives the mean temperature coefficient values for the three classes of material plotted against maximum induction. The data for the large samples are included.

Fig. 5 gives the same data plotted against maximum magnetizing forces.

Fig. 6 gives the average permeability in percent of the 20°C values plotted against temperature for the three classes of material and for a maximum induction of 10 kilogausses. Since the maximum negative temperature coefficient occurs at about 10 kilogausses, these lines have approximately maximum negative slope. For other inductions the slopes will be less or in the case of medium and low-silicon steels the the slopes will reverse for the lower inductions.

Discussion of results. It will be seen from Fig. 3 (and this is corroborated by data not shown) that the samples for a given grade of material all have about the same temperature coefficient characteristics. The

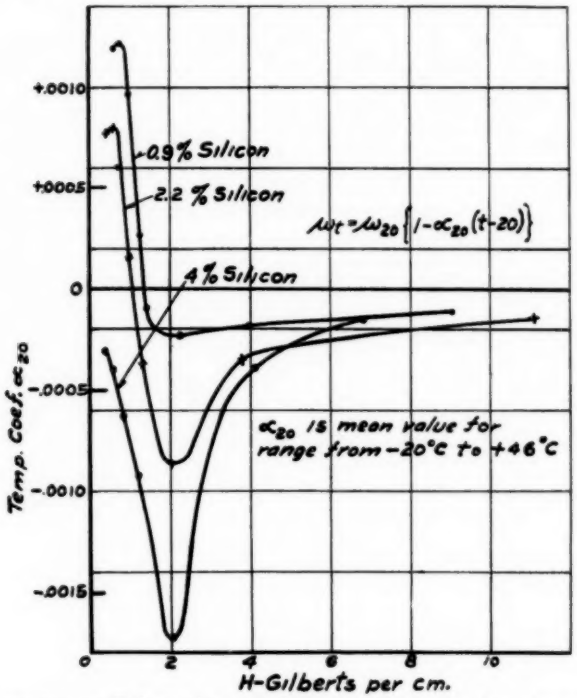

Fig. 5. Temperature coefficient of magnetic permeability as a function of magnetizing force, based on the permeability at 20°C.

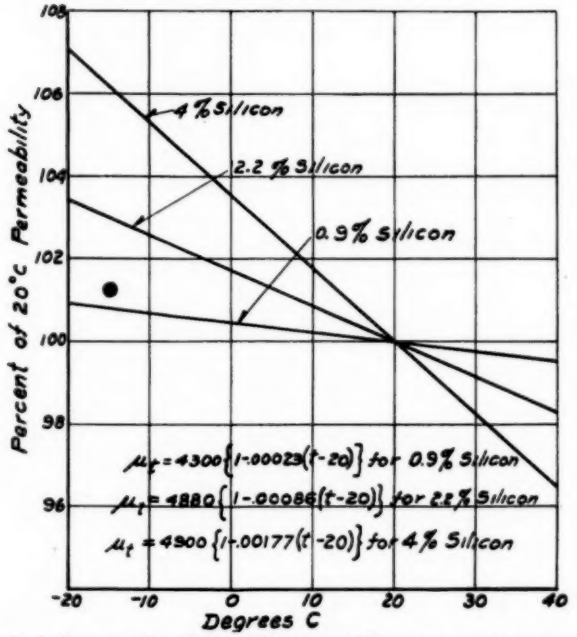

Fig. 6. Electrical sheet steel. Change in permeability due to temperature, based on permeability at 20°C. $B_m = 10$ kilogausses.

large samples show slightly different characteristics, particularly in the case of the 4 percent silicon steel. This may be due to the fact that the effect of punching alters the temperature coefficients, even after annealing.

The change of sign of the temperature coefficients with induction is common to many types of ferro-magnetic materials. The cause is an interesting subject for speculation. It might be expected that the maximum negative temperature coefficients would occur at the same inductions as those at which the maximum permeability occurs or at least that the temperature coefficient curves against the flux density would show some definite change corresponding to these inductions. However, this does not seem to be the case. There seems to be no definite relation between permeability and temperature coefficient. The maximum negative temperature coefficients correspond quite definitely to approximately 10 kilogausses whereas the maximum permeabilities occur at about 6 or 7 kilogausses.

Conclusions. From these data and others not included, the following conclusions may be drawn.

1. Low and medium silicon steels have large positive permeability temperature coefficients for low inductions and negative coefficients for high (up to 14 kilogausses). Four percent silicon sheet on the average has negative coefficients for all inductions (up to 14 kilogausses) though individual samples may have small positive coefficients for low inductions.

2. As the silicon content increases, the coefficients tend to move in a negative direction. This may be due to the direct influence of the silicon or to an indirect influence of the silicon on the carbon and other impurities.

3. The shape of the temperature coefficient curves seems to be much more definitely a function of the induction than of the m.m.f., since the maximum negative temperature coefficients correspond very definitely to a certain induction but may vary over a considerable range of m.m.fs.

4. There seems to be no definite relation between permeabilities and temperature coefficients for the individual samples of a particular grade of material and no definite relation between the inductions at which maximum permeabilities and maximum temperature coefficients occur.

WESTINGHOUSE RESEARCH LABORATORY,
EAST PITTSBURGH, PA.
September 10, 1925.

THE PROPAGATION OF RADIO WAVES OVER THE EARTH

By A. Hoyt Taylor and E. O. Hulburt

Abstract

Theory of radio wave propagation over the earth.—Larmor's theory of refraction due to the electrons of the Kennelly-Heaviside layer does not explain the "skip distances" for short radio waves (regions of silence around the transmitter which Taylor's measurements showed to be 175, 400, 700 and 1300 miles in radius in the daytime for waves of 40, 32, 21 and 16 meters, respectively, and which are surrounded by zones of strong signals). The range as a function of wave-length shows a minimum for about 200 meters which suggests the introduction of a critical frequency term. If the effect of the magnetic field of the earth on the motion of the electrons is taken into account, as suggested by Appleton and by Nichols and Schelleng, the modification of the Larmor theory necessary to fit it to the experimental facts is secured. A quantitative theory is here developed. The upper atmosphere is assumed to contain N free electrons per cc., and neglecting absorption the dispersion equations are worked out for various modes of polarization of the radio waves. Then the skip distances are computed, making various assumptions as to the electron density distribution. (a) Reflection theory. As a first approximation the layer is taken to be sharply separated from the un-ionized lower atmosphere. At this layer total reflection occurs in accordance with Snell's law. (b) Refraction theory. The following distributions are considered: (1) Density increasing linearly with the height h, beginning at a certain height h_0; (2) Density proportional to h^2; (3) Density proportional to e^h; (4) Density proportional to $h^{\frac{1}{2}}$. Comparison with the experimental skip distances shows good agreement, and indicates that the radio waves which just reach the edge of the zone beyond are refracted around a curved path, reaching in the daytime a maximum height of from 97 miles (case 1, $h_0=21$ miles, and case 2) to 149 miles (case 3). At this height the electron density comes out close to 10^5 electrons per cc. At night the electron density gradient is less and the height is greater. These conclusions agree with physical conceptions from other evidence. From the dispersion equations it follows that for waves of 60 to 200 meters, total reflection may occur from the electron layers at all angles of incidence. From this result, combined with interference between various modes of polarization of the radio rays, a detailed qualitative explanation of many fading phenomena is presented. Further conclusions are: That the ions in the atmosphere have little effect in comparison with the electrons; that for longer waves, the Larmor theory is correct; that short waves are propagated long distances by refraction in the upper atmosphere and reflection at the surface of the earth, not by earth-bound waves; that waves below 14 meters cannot be efficiently used for long distance transmission.

Introduction

THE conception that upper regions of the atmosphere of the earth relatively richer in ions and electrons than the lower levels may play an important role in the propagation of radio waves over the

earth has become more firmly established with the years. It is the purpose of this paper to develop the conception in greater detail than perhaps has been done up to this time and to discuss the conclusions quantitatively in the light of new experimental observations on the transmission of short radio waves over long distances. The first suggestion[1] of ionized atmospheric layers in connection with radio waves was, as far as we know, published by Kennelly.[2] Heaviside[3] set forth similar ideas independently a few months later. We have therefore thought it correct to speak of the ionized layer as the "Kennelly-Heaviside layer," although the designation "Heaviside layer" has been widely used in the literature of radio.

Although no complete summary of the researches on electric wave propagation will be attempted here, a few of the more important steps may be outlined briefly. Our experimental knowledge of the variation of the strength of the received signal as the distance from the transmitting station is increased is due largely to the work on waves longer than 500 meters carried out in 1910 and 1913 by the United States Navy under the direction of Austin.[4] The results are usually expressed by the well-known Austin-Cohen formula, which showed, in particular, that the intensity of the received wave fell off faster than the distance from the source than would be required by a simple inverse square law. The mathematical researches of Nicholson,[5] Love,[6] and Van der Pol,[7] Macdonald,[8] Watson,[9] and others have led to the conclusion that a simple theory of diffraction of the waves around an earth of finite, or infinite, conductivity immersed in a limitless dielectric yielded an intensity decrement factor very much greater than the experimental factor of the Austin-Cohen formula. In order to obtain agreement with observations the presence of converging waves was necessary, which meant that a portion, at least, of the waves must be reflected or refracted downward from the ionized upper reaches of the atmosphere. This was in strong support of the Kennelly-Heaviside conception which just at that time had been given a more definite formulation by

[1] See L. Bouthillon, L'Onde Électrique **2,** 345 (1923).

[2] Kennelly, Electrical World and Engineer, p. 473 (March 15, 1902).

[3] Heaviside, Encylopædia Britannica, Tenth Edition, Ninth Volume (No. XXXIII), p. 215 (December 19, 1902).

[4] Austin, Bull. Bur. Stand., **7,** 317 (1911).

[5] Nicholson, Phil. Mag. **22,** 157 (1910); **21,** 62 (1911).

[6] Love, Phil. Trans. Roy Soc. A, **215,** 105.

[7] Van der Pol, Phil. Mag. **38,** 365 (1919).

[8] Macdonald, Proc. Roy. Soc. **71A,** 251 (1903).

[9] Watson, Proc. Roy. Soc. **95A,** 546 (1919).

Eccles.[10] Eccles assumed an upper layer so intensely ionized as to reflect the rays without penetration, combined with an ionization of the middle atmosphere which bent them, and in his treatment dealt only with the motions of the heavy ions. It has remained for Larmor[11] in an interesting paper of accustomed clarity, to sketch a theory of refraction due largely to the free electrons. These were shown to be of such long free path as to exert a negligible absorption on the waves passing through them. Being lighter than the ions of Eccles only comparatively few electrons were necessary to produce sufficient bending of the rays.

At the end of the year 1924 it appeared that a reasonable and adequate theory of radio wave propagation had been rounded out, as yet qualitative to be sure, but requiring only obvious measurements to be placed on a quantitative basis. At this satisfactory stage, as has often happened before, new phenomena made their appearance which the theory was unable to cope with. Larmor's equations gave a refraction which decreased with the wave-length becoming small for waves below 60 meters, whereas the work of Reinartz[12] and Taylor[13] on the "skip distance" for waves below 60 meters immediately indicated a stronger refraction than for the long waves. Fortunately, at this time Appleton[14] pointed out that the free electrons would move in spiral paths at a specified frequency because of the magnetic field of the earth, and that perhaps peculiar effects would occur for waves near this frequency. This meant of course the introduction of a critical frequency term into the refraction equation, which produced exactly the modification required, i. e., it left Larmor's equations (which had neglected the magnetic field of the earth) approximately unchanged in the region of longer waves and brought the theory into agreement with the short wave data. It may be mentioned that we had already independently introduced a critical frequency term into the classical dispersion formula used by Larmor, basing the idea on the curve of Fig. 2, without however troubling as to the physical cause of the term. From Appleton's suggestion it was immediately possible to apply the classical formulas of magneto-optics to the Kennelly-Heaviside layer. While this was in progress the paper of Nichols and Schelleng[15] appeared in which similar ideas, again of independent origin, were taken up. However, this paper and theirs do not cover the same ground, for

[10] Eccles, Proc. Roy. Soc. **87A, 79** (1912).
[11] Larmor, Phil. Mag. **48,** 1025 (December, 1924).
[12] Reinartz, "QST" **9,** 9 (April, 1925).
[13] Taylor, Proc. Inst. Radio Eng. **13,** 677 (December, 1925).
[14] Appleton, Proc. Phys. Soc. London **37,** Part 2, p. 22D (February, 1925).
[15] Nichols and Schelleng, Bell System Techn. J. **4,** 215 (April, 1925).

in their paper no quantitative applications of the formulas to observations were made. The publication of this paper* has been delayed until the results of the observations on the secondary skip distances were available.

Data from Taylor's Range Chart

The observational data of interest in the present development are to be found in Taylor's Range Chart,[13] which presents in graphical form a summary of a large number of experimental observations on the transmission of radio waves of wave-lengths from 16 to 3000 meters over distances up to 10,000 miles. The experiments have been carried out during recent years by the Radio Division of this laboratory with the assistance of the American Radio Relay League and their coworkers in the foreign countries. On the chart, which is not reproduced here, are plotted the relative ranges of transmission of the various wave-lengths, as far as they have been investigated, reduced to a uniform condition, namely, 5 kilowatts in a normal transmitting antenna. The average ranges for day and night and for summer and winter are included.

From the chart certain new facts regarding the behavior of the short waves stand out. It has been found that for wave-lengths shorter than 50 meters the intensity of the received signal decreased as the distance from the transmitter was increased, reaching a value too small to be observed at a distance of a hundred miles or so. With further increase of distance the received signal remained undetectable until a region was reached where the received signal became strong again, rising rapidly to a maximum and thereafter decreasing rather slowly. The distance from the transmitter to the far edge of the region of silence, which we may call the "skip distance," was found to increase rapidly as the wave-length decreased; for a specified wave-length it was longer at night than in the day and longer in winter than in summer. The skip zone was not very sharply defined of course, but passed into the region of steady signals through a transition zone, sometimes called the "flicker" zone, where the signals were erratic and subject to violent fading. It may be emphasized that the skip zone was not merely a zone of uncertain signal reception, but a region where the signals were entirely absent for the most part; a conservative estimate would be that the intensity of the signal at a point three fourths of the distance out into the skip zone was at least 10^{-4} of the intensity of the signal

* A preliminary abstract of the present paper appeared in Science, p. 183 (August 12, 1925).

zone beyond. The skip distances, denoted by $2s$, averaged throughout a year, for full daylight conditions, for wave-lengths 16, 21, 32 and 40 meters were 1300, 700, 400 and 175 miles, respectively. These are plotted as rectangles in Fig. 1. The values naturally can not claim great accuracy and may perhaps be in error by as much as a hundred miles. The skip distances at night are not yet known with precision. This is due perhaps to an insufficiency of data, but more probably to the fact that conditions at night are so erratic that even more extended observations would fix the distances only within wide limits. Present information indicates, however, that the night skip distances are on a rough average three or four times the corresponding day values.

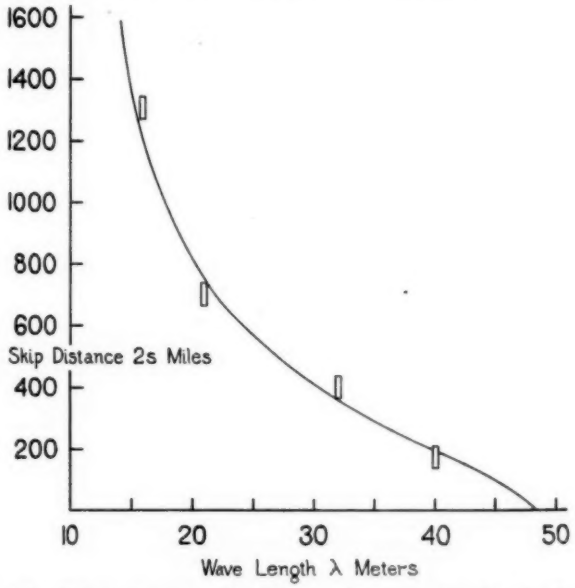

Fig. 1. The skip distances averaged throughout a year, for full daylight conditions, as a function of wave-length.

We regard these skip distance phenomena as demonstrating forcibly that two portions of the transmitted wave may be differentiated, one which clings to the earth and decreases rapidly in intensity until it is lost, and the other which moves in an upward direction and returns to the earth after refraction, with little attenuation in the Kennelly-Heaviside layer.

In Fig. 2 are plotted the ranges, under full daylight conditions, averaged throughout a year for uniform transmitting conditions, i. e. 5 kilowatts in a normal transmitting antenna, against the corresponding wave-lengths. Although the physical basis of the curve is essentially composite, for each wave-length may be propagated in a characteristic

manner, the pronounced minimum in the curve at about 200 meters is taken to suggest a critical region of dispersion or of absorption. The agreement of the position of the minimum with the calculated critical wave-length 214 meters (§6) gives reality to this suggestion.

Dispersion Equations of a Magnetized Electron Gas

3. It is assumed that the regions of the Kennelly-Heaviside layer owe in the main their optical properties to the presence of the free electrons, and in the equations the influence of the magnetic field of

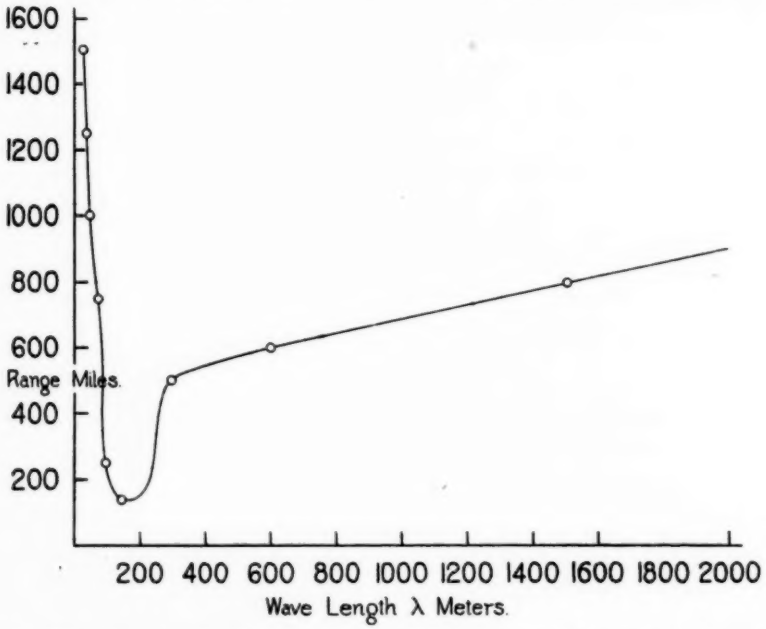

Fig. 2. The ranges, under full daylight conditions, averaged throughout a year, for uniform transmitting conditions, as a function of wave-length.

the earth is taken into account. We follow the classical electron theory of Lorentz,[16] and in application to the present problem we assume no restoring force on the electrons due to the medium, no absorption, and no effect of the electrons on each other; this amounts to placing a, f and g equal to zero in equations (198) (see Lorentz, loc. cit.,[16] p. 139). Let ξ and E_x be the X components of the displacement of the electron from its equilibrium position and the electric force, respectively, and η, ζ, E_y and E_z the Y and Z components of the quantities. The charge on the electron is denoted by e, its mass by m; N is the number of

[16] H. A. Lorentz, "The Theory of Electrons," Chapter IV (1916).

electrons per unit volume. The magnetic permeability of the medium is taken to be unity. All quantities are expressed in c.g.s., e.m. units.

4. *Propagation parallel to the magnetic field.* This case will apply approximately to North and South propagation. We denote the magnetic field by H and suppose it to have the direction of the axis of Z, which is also the direction of the propagation of the radiation. We take the radiation to be initially plane polarized. In Newtonian notation the equations of motion of the electrons are

$$\left.\begin{aligned} m\ddot{\xi} &= eE_x + He\dot{\eta}\,, \\ m\ddot{\eta} &= eE_y - He\dot{\xi}\,, \\ m\ddot{\zeta} &= eE_z\,. \end{aligned}\right\} \tag{1}$$

Let ϵ be the base of natural logarithms, and let all dependent variables of (1) contain the time only in the factor $\epsilon^{i2\pi tc/\lambda}$ where c/λ is the frequency, c is the velocity of light in vacuum, and i is $\sqrt{-1}$. The solution of (1) yields two vibrations circularly polarized in opposite directions, whose refractive indices μ are given by the relations

$$\mu^2 = 1 - \frac{C\lambda^2}{1-\lambda/\lambda_0}\,, \tag{2}$$

$$\mu^2 = 1 - \frac{C\lambda^2}{1+\lambda/\lambda_0}\,, \tag{3}$$

where

$$C = Ne^2/\pi m \text{ and } \quad \lambda_0 = 2\pi cm/He\,. \tag{4}$$

The details of this solution are here omitted for they are essentially the same as those given by Lorentz. If the refraction is not great or the distance of propagation is small the wave remains coherent and the two circularly polarized components add to give in general an elliptically polarized wave. For equal intensities of the two components the resultant wave is plane polarized with the plane of polarization rotated from its original direction. If the two components are separated, by greater refraction or distance, each will proceed as a circularly polarized wave.

5. *Propagation perpendicular to the magnetic field.* In this case, which will refer approximately to East and West propagation, the initially plane-polarized wave is resolved in general into two component vibrations with electric vectors parallel and perpendicular to H, respectively. The solutions of the appropriate equations of motion of the electron

yield refractive indices μ for the parallel and perpendicular cases, respectively,

$$\mu^2 = 1 - C\lambda^2 , \tag{5}$$

$$\mu^2 = 1 - \frac{C\lambda^2}{1 - \lambda^2/\lambda_0^2(1 - C\lambda^2)} . \tag{6}$$

If the wave remains coherent the two plane vibrations unite to produce in general an elliptically polarized wave, but if the two components are separated, each will proceed as a plane polarized wave. Eq. (5) of course represents the propagation in the absence of a magnetic field as discussed by Larmor. It may be mentioned in passing, although no use is made of the fact here, that for the plane polarized wave component of formula (6) the electrons describe ellipses whose planes are parallel to the direction of propagation of the wave and perpendicular to H. From one point of view these vibrations can not be said to be transversal. This peculiar instance was recognized long ago by Voigt. The case may be compared with the motion of the particles on the surface of deep sea waves on water.

6. In the general case of propagation at an angle with the magnetic field all four of the modes of vibration just discussed may occur in greater or less proportion, with the result that the wave, if coherent, will become elliptically polarized, the orientation of the axes and the eccentricity of the ellipse changing as the wave proceeds. If the refraction or distance of propagation is sufficiently great the various components may be separated from each other.

Taking the value of H for the earth's magnetic field to be 0.5 gauss, λ_0 from (4) comes out to be 214 meters. This is the value calculated by Nichols and Schelleng (loc. cit.) and is the value used for λ_0 throughout this paper. The minimum at about 200 meters of the curve of Fig. 2 agrees closely with $\lambda_0 = 214$ meters. This is regarded as an experimental confirmation, indirect of course, of the theoretical calculation.

To bring out the characters of the various dispersion formulas the curves 2, 3, 5 and 6 have been plotted in Fig. 3 from Eqs. (2), (3), (5) and (6) respectively, choosing $N = 3.95 \times 10^5$ electrons per cc. In the region of wave-lengths less than 50 meters the curves do not differ greatly. With increase in λ all the curves of Fig. 3 descend to zero and μ becomes imaginary, remaining so for the longer waves in the case of curves 3 and 5. For curves 2 and 6 μ remains imaginary until wave-lengths λ_0 and $\lambda_0\sqrt{1 - C\lambda^2}$ are reached, respectively. At these wave-lengths, called the "critical" wave-lengths, μ is $\sqrt{\pm \infty}$ and as λ is increased beyond them μ descends from high positive values

finally to low values again. As a matter of fact the critical wave-length $\lambda_0\sqrt{1-C\lambda^2}$ appears to be of no physical importance, for, due to the presence of C in this expression, no wave can reach the region of electron density where this critical condition for the wave prevails.

7. *Absorption in the Kennelly-Heaviside layer.* Among various possible causes of absorption of energy from the electromagnetic wave by the upper reaches of the atmosphere the most important would seem to arise from collisions between electrons and molecules. This would

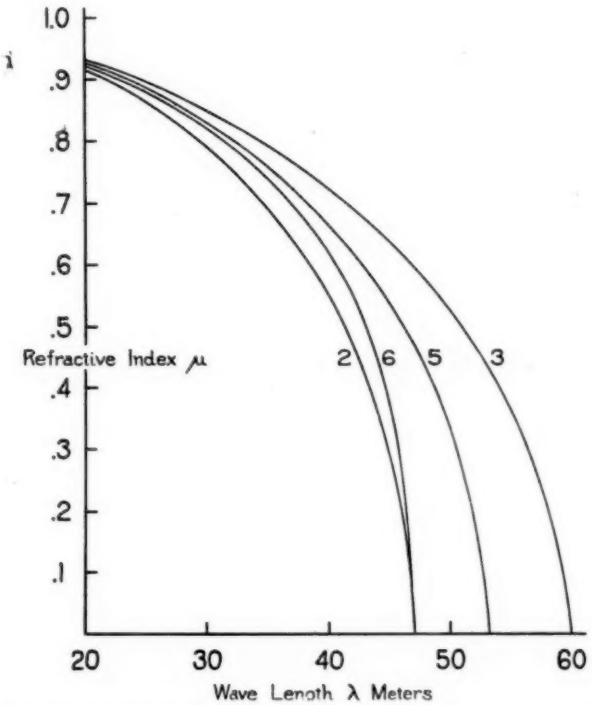

Fig. 3. Refractive indices of the Kennelly-Heaviside layer as a function of wave-length for rays in and perpendicular to the direction of the earth's magnetic field (Eqs. (2), (3), (5), (6)).

convert a portion of the energy of the wave into heat. Simple calculations, such as given by Larmor and by Nichols and Schelleng, indicate that the probability of collision is small, so that absorption due to this cause is negligible, except in the region near the critical wave-length λ_0 and for very long waves outside of the usual radio range, which have a very slow oscillation. In lower regions of the atmosphere, where the density of molecules is greater, absorption due to collision might exist even for shorter waves. If we assume that this type of absorption can be

expressed as a frictional term in the equations of motion of the electron, which is no doubt permissible within limits, the dispersion formulas are all available in treatises on magneto-optics. For small absorption these differ from Eqs. (2), (3), (5) and (6) by wholly inappreciable amounts for wave-lengths removed by, say, 30 meters from $\lambda_0 = 214$ meters. Near to this critical region the absorption term produces complex modifications, which have been discussed by Nichols and Schelleng. It is, however, justifiable to neglect absorption as long as the critical region is avoided; and we have been content to avoid this region because of its complexity and because the observations on these wave-lengths are mainly qualitative.

For a wave traveling near the earth the matter of absorption is quite different. This has been discussed by Zenneck,[17] Sommerfeld and others who showed that the earth absorption may become very high for the shorter waves. The successful radio transmission to distances as great as half-way around the earth with waves below 90 meters proves that the attenuation is small, no matter to what cause it is attributed, and this combined with the pronounced earth absorption for the shorter waves leads forcibly to the conclusion that the waves must travel in the upper atmosphere and that the absorption in these regions is slight.

Reflection Theory

8. It is assumed that the lower levels of the atmosphere of the earth are relatively free from electrons and that the lower surface of the Kennelley-Heaviside layer, the region of relatively great electron density, is sharply marked. A radio ray transmitted in an upward direction would travel in a straight line and after reflection from the layer would return in a straight line to the earth. Actually, of course, the optical constants of the lower atmosphere merge without discontinuity into those of the electronic regions, so that a ray instead of being sharply reflected is refracted along a curved path. As often happens in theoretical physics, we consider first the simple case of sharp reflection and then pass to a refraction theory which is probably more in accord with the real state of things. Moreover, many of the conclusions of the reflection theory are found to be unchanged for the refraction theory.

We take the lower boundary of the layer, represented by AE in Fig. 4, to be a spherical surface parallel to the surface of the earth and at a height h above the earth. The radius of the earth is R. Let CAF

[17] Zenneck, "Wireless Telegraphy," 3rd Ed., p. 248 (1915).

be the path of a radio ray transmitted from C which is reflected from A at an angle ϕ and let the length of the arc CF be $2s$; s subtends the angle θ at the center of the earth. *It is now assumed that when $2s$ is the observed skip distance for a specified wave-length ϕ is the critical, or Snell, angle of total reflection of the wave from the layer.* Since the refractive index of the atmosphere below the layer is unity this assumption of course involves the condition that the refractive index of the layer is less than unity for those wave-lengths for which a skip distance exists. Otherwise a critical angle of total internal reflection would be impossible and no skip zone would exist. If μ is the refractive index of the Kennelly-Heaviside layer, then from Snell's Law,

$$\mu = \sin \phi \ . \tag{7}$$

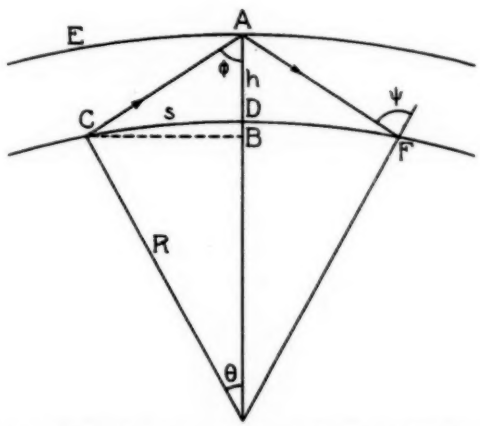

Fig. 4. Reflection from the Kennelly-Heaviside layer.

From the geometry of Fig. 4,

$$\sin \phi = CB/AC = R \sin \theta / \left\{ R^2 \sin^2 \theta + (R + h - R \cos \theta)^2 \right\}^{1/2} \tag{8}$$

and

$$s = R\theta \ .$$

The discussion is limited for the moment to the special case of dispersion represented by Eq. (2). When this equation was combined with (7) and (8) to eliminate ϕ and θ there resulted a relation between the unknown quantities h and C, the known constants R and λ_0, and the observed quantities λ and s. The substitution of the observed skip distances $2s$ for wave-lengths 16 and 40 meters into this relation yielded two equations in h and C. Eliminating C from these led to a quartic equation in h, which determined h and thence C. with these values of h and C, with $R = 3970$ miles and with $\lambda_0 = 214$ meters the $2s,\lambda$ curve was plotted and readjusted to approximate a least square solution.

The final $2s,\lambda$ curve is shown in Fig. 1, and the values of h and C corresponding to this curve were 152 miles and 3.54×10^{-8}, respectively. With this value of C in (4) together with the usual values of the electronic mass and charge, N came out to be 3.95×10^{5}. The agreement between the theoretical curve and the observed values in Fig. 1 is regarded as a confirmation of the correctness of the theory. Further, the values of h and N which have emerged appear reasonable. h is well within the aurora domain which, according to Stormer[18] is between 50 and 300 miles above the earth. In this region where the pressure may be of the order of 10^{-5} atmospheres a simple calculation indicated that an electronic density of the order of 10^{5} per cc. is easily possible, the electrons supposedly being caused mainly by the ultraviolet light of the sun. The values for N and h appeared to be quite definitely established as far as the present theory and calculations were concerned, for a variation in them of as little as 20 percent gave rise to discrepancies between the calculated and observed skip distances. Further, N and h did not depend at all critically on the value chosen for λ_0, changing, for example, by only a few percent when λ_0 was varied from 120 to 300 meters. The reason for this lay in the nature of the dispersion equation (2), and the fact that the wave-lengths below 60 meters were remote from the critical wave-length λ_0. It would therefore appear that N and h and the refraction of the rays are little influenced by time or space variations in the earth's magnetic field.

9. The dispersion curve, μ against λ, plotted from Eq. (2) with $\lambda_0=214$ meters and $N=3.95\times10^{4}$, is shown by curve 2, Fig. 3. The Snell angles ϕ calculated by means of (7) for wave-lengths 16, 21, 26, 32 and 40 meters were 71.8, 65.2, 58.4, 49.2 and 33.4 degrees, respectively. The angles which the direction of the down-coming wave at the edge of the skip zone makes with the vertical are for the respective wave-lengths 79.5, 70.6, 62.1, 51.8 and 34.8 degrees. These were calculated from the relation $\psi=\phi+\theta$ (see Fig. 4). An experimental determination of these angles would offer direct evidence concerning the present theory. In such experiments complicating effects of the ground at the receiving station should be avoided or recognized.

Since h is roughly proportional to s, the fact that the night skip distances are about three times the day values indicates that h at night is three times the day value. The angles ψ will be greater at night than in the day by amounts corresponding to the change in θ.

10. Because of the bulge of the earth and the curvature of the layer, the curve of Fig. 1 ceased to exist at wave-length 14 meters. The

[18] Stormer, Proc. Phys. Soc. London, **37**, part 2, 50 D (1925).

Snell angles for wave-lengths shorter than this being so nearly 90° that even rays transmitted horizontally from the surface of the earth could not be totally reflected from the layer. Since it appears that the overhead reflected (or refracted) wave and not the ground wave is all-important in long-distance short wave radio transmission, *the present theory indicates that communication over long distances by means of wave-lengths less than 14 meters will be relatively difficult.* This is due to the mechanism of the propagation entirely apart from the inherent technical difficulties in the apparatus for producing these very short waves with appreciable intensity. The few experiments which have been made in this region support this conclusion; for example, no long distances have been reached in the case of tests with 5 meter waves. It is hardly necessary to remark that due to unusual ultra-atmospheric conditions, etc., long distance communication with very short waves may be successful at times. Such cases should prove to be the exception rather than the rule.

11. The foregoing calculations have been based on dispersion equation (2) which refers to one of the circularly polarized waves arising from propagation along the magnetic field. They are, furthermore, valid and accurate, within limits, for the general case of propagation of a wave with electric vector at a random and changing angle to the magnetic field, because the general case differs but slightly from the special case in the region of wave-lengths below 40 meters. This is evident when the μ,λ curves for the various dispersion equations, Eqs. (2), (3), (5) and (6), are compared. These are plotted in Fig. 3, curves 2, 3, 5, and 6 respectively, using the constants $\lambda_0 = 214$ meters and $N = 3.95 \times 10^5$ or $C = 3.54 \times 10^{-8}$. For wave-lengths below 40 meters the refractive indices for the various curves are closely the same, and hence the Snell angles and the skip distances are approximately the same. In this connection curve 3 may be disregarded for it refers to one of the component waves of propagation parallel to the magnetic field and wherever this exists the other component represented by curve 2 also must exist. The skip distances from curve 2 are all less than those from curve 3 and are therefore the ones which would be observed. The cases of propagation which differ most widely are, then, those represented by curves 2 and 5. These yield skip distances which differ by about 60 miles, those from curve 5 being the greater. If Eq. (5) instead of (2) had been used h and N would have come out roughly 10 percent different from the values for (2). Therefore the values of h and N, which have been determined from curve 2, may be considered to be sufficiently accurate for the general case, which lies

somewhere between the conditions of the curves 2 and 5; especially so, since the values can only be looked upon as rough averages of quantities which probably vary each moment of the day throughout the year. It follows at once from the approximate sameness of curves 5 and 6 which refer roughly to East and West propagation, and of curve 2, which refers to North and South propagation, that the skip distances do not vary appreciably with the compass direction of propagation. This is in accord with the experimental observations.

In the band of wave-lengths between 50 and 60 meters the curves of Fig. 3 suggest an appreciable variation in skip distance with the mode of propagation. For example, if the conditions of curve 3 obtained, we might expect a skip distance of 120 miles for a 50 meter wave, whereas under the conditions of curve 2 no skip distance would exist. There is some evidence that this effect exists although the observations are none too certain because of the ground wave which may fill in the skip region. However, there is noticed at times an unusual flickering in the intensity of signals in this region which farther away are stronger and steadier.

12. Up to this point we have mentioned only the contribution of the electrons to the dispersion in the upper atmosphere, and we may now show that the more massive ions have little influence. In the dispersion formulas (2), (3), (5) and (6) the effect of the ions on μ may be calculated to a first approximation by adding another term (or terms, there being a term for each type of ion) similar to the last term of each equation, using the mass of the ion instead of the electron, which for, say, a nitrogen ion is 10^4 greater. The quantity $C = Ne^2/\pi m$ in the numerator of the ionic term is then 10^{-4} of the corresponding quantity for the electronic term for the same density of ions and electrons, the denominators being approximately the same for short waves. Therefore the ionic term will be negligibly small compared to the electronic term, except for very long waves outside of the usual radio range unless there are at least 10^8 as many ions as electrons. Such a preponderance of ions is hardly to be expected in general. In view of this and of the good agreement of the theory with the observations, as indicated in Fig. 1, the conclusion may be emphasized that *the reflection (or refraction) of radio waves in the layer is caused in general by the electrons and not by the more massive ions.* This may be regarded as a definite proof of the presence of considerable numbers of electrons in the upper atmosphere of the earth.

Refraction Theory

13. The physical conditions in the upper atmosphere are scarcely such as to render tenable a theory of reflection, for the transition from

the low electron density of the lower atmosphere to the higher concentration of electrons in the Kennelly-Heaviside layer must be gradual and not abrupt. We therefore pass to a theory of refraction as offering a more exact picture of actual conditions, with the preliminary remark that the results of the refraction theory are for the most part identical with those of the reflection theory. This is to be expected since reflection is only a special case of refraction. We must now call attention to a circumstance which throws further doubt on a reflection theory and which supports a refraction theory. If we suppose, as has been done, that the edge of the skip zone marks the Snell angle of total reflection then, as we pass into the skip zone to points where reflection occurs at angles less than the critical angle, the reflected intensity will become less, but will not drop to zero, and in the case of rather oblique incidence, as with the 16 meter wave, the reflected intensity may be decreased by only a few percent. It would therefore follow that the intensity of the signals would drop off very slowly as the skip zone was entered never reaching low values except at nearly normal incidence, and even there not zero. It is well known, on the contrary, that the signal intensity at, say, a distance of one fourth of the way in from the outer edge of the skip zone, is less than 10^{-4} of the intensity in the region beyond the skip zone. This discrepancy in the case of the reflection theory does not occur for the refraction theory.

The calculations become much simpler if we consider the case of a flat earth instead of the curved earth discussed heretofore. For a flat earth Eq. (8) of the reflection theory becomes

$$s = h \tan \phi \tag{9}$$

which is of course a close approximation to (8) for short distances, up to 1000 miles. It will be shown later, however, that entirely apart from this approximation, the flat earth calculation can be referred to a curved earth with exactness.

The elaboration of a refraction theory requires the determination of the ray-paths of the wave, and these may not be determined explicitly without a knowledge of the variation of the optical constants of the atmosphere with the distance above the earth. The method of procedure has thereupon consisted in assuming a number of types of this variation and in investigating the results of these assumptions.

14. It is assumed that the surface of the earth is flat and that the refractive index μ of the region lying above the earth is a function of y and not of x, where Y and X are the coordinate axes in the vertical and horizontal directions, respectively. μ is assumed finite, single-valued and continuous for a specified wave throughout the region. Let ABC,

Fig. 5, be the ray which is projected from a point A on the surface of the earth at an angle ϕ with the vertical let μ_0 be the refractive index of the atmosphere at A. Let adjacent elements on either side of a point B on the curve make angles i and $i+di$ with the vertical, and let the refractive indices at these elements be μ and $\mu+d\mu$, respectively. Then, from Snell's Law

$$(\mu+d\mu)/\mu=(\sin i)/\sin(i+di).$$

Whence

$$\mu=a/\sin i,$$

where a is a constant of integration. From the initial conditions $\mu=\mu_0$, $i=\phi$, we obtain

$$a=\mu_0 \sin \phi \tag{10}$$

and

$$\mu=(\mu_0 \sin \phi)/\sin i \tag{11}$$

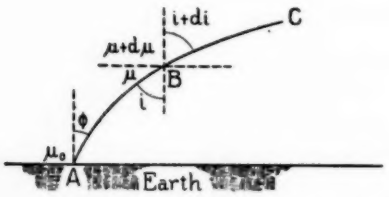

Fig. 5. Refraction of a radio ray in an electron atmosphere of variable density.

This is Snell's Law generalized for the present problem. Since (11) must be satisfied at every point of the ray-path, the differential equation of the path is

$$dy/dx=-\cot i=-\sqrt{(\mu^2-a^2)/a^2} \tag{12}$$

where $\mu=f(y)$ and a is independent of x and y. This may not be integrated explicitly and therefore the equation of the ray-path can not be determined, unless $\mu=f(y)$ is known. In order to proceed farther various assumptions as to $f(y)$ are made and investigated in the following paragraphs.

15. *Case 1. Electron density proportional to height.* It is assumed that the electron density sets in at the surface of the earth and increases proportionally with the height above the earth. We write

$$N=\beta y \tag{13}$$

where N is the electron density at a point y cm above the surface of the earth. Then, from (3) for each of the dispersion formulas (2), (3), (5), and (6),

$$\mu^2=1-\gamma y \tag{14}$$

where γ is determined by identifying (14) with each dispersion formula in turn. At the surface of the earth $y=0$ and from (14) $\mu=1$. Therefore, from (10)

$$\alpha=\sin\phi. \tag{15}$$

Introducing (14) into (12) and integrating gives for the equation of the ray-path,

$$x^2=\{4\alpha^2(1-\alpha^2-\gamma y)\}/\gamma^2. \tag{16}$$

This is a parabola. The constant of integration has been eliminated by a shift of the curve along the X axis. The maximum height h above the earth reached by the ray is

$$h=(1-\alpha^2)/\gamma. \tag{17}$$

The ray comes down to the earth again at a distance $2x_0$ from its starting point, where

$$x_0=2\alpha\sqrt{1-\alpha^2}/\gamma\ . \tag{18}$$

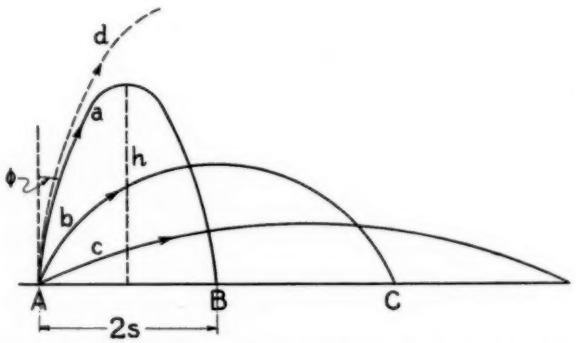

Fig. 6. Refraction of radio rays transmitted from A at varying angles through an electronic atmosphere whose density is proportional to the height.

Combining (18) with (15) and (17) leads to

$$x_0=2h\tan\phi\ . \tag{19}$$

The ray-paths plotted from (16) for a specified wave transmitted from A, Fig. 6, at increasing angles ϕ are illustrated by curves a, b, and c, Fig. 6. It is seen that as ϕ increases h decreases and $2x_0$ increases. *We may now identify AB, the distance between the feet of curve a, as the skip distance for the wave in question.* This means that any other ray such as d, whose angle of projection ϕ is less than that of ray a, will not return to the earth between points A and B; it may possibly return at some distant point or perhaps not at all. It follows, therefore, that the law of electron distribution given by (13) ceases to hold above the summit of curve a. Just what will be the law above h is of course

unknown, but this much can be said, that the electron density must increase less rapidly above h than it did below h. *Therefore the "height of the Kennelly-Heaviside layer" means merely the distance above the earth to the region where the rate of increase in the electron density with the height becomes less. And because of its physical appeal, in spite of other mathematical possibilities, we take this region to be the region of maximum electron density.*

According to the supposition just made that AB of curve a, Fig. 6, be the skip distance for the wave, formula (19) becomes

$$s = 2h \tan \phi . \tag{20}$$

We might now introduce the observed skip distances into (20) and from the relation $\mu = \sin\phi$ at the height h and one of the dispersion equations determine h and N, just as was done in the case of reflection. It is not necessary to do this, however, because of the similarity of (20) and (9). It is seen that these formulas, which refer to a flat earth, are the same except that h of (20) is one-half h of (9). We may therefore conclude that if the skip distance refraction formula for a curved earth corresponding to (20) had been developed, it would be nearly the same as (8) which is the reflection formula for a curved earth corresponding to (9). This is true because only matters of geometry enter into the transformation from a curved to a flat earth. We may finally conclude that *all the numerical facts of this refraction case are exactly the same as those which have been derived from the reflection theory, except that h is one-half the h of the reflection theory.* h is now 76 miles, but N, the calculated $2s,\lambda$ curve, the angles at which the rays at the edge of the skip zone descend to the earth, etc., are as before.

We may now emphasize the contention stated in §13, which pointed out that within the skip zone the intensity of the received signal is known to be 10^{-4} or less of the intensity in the surrounding signal zone. The refraction theory is in accord with this, for referring to Fig. 6, there is no ray-path possible which connects the transmitter A with a receiver inside the skip zone.

16. *Case 1a.* The assumption of (13) and the result that for $y = 76$ miles $N = 3.95 \times 10^5$ electrons per cc is scarcely possible, for this would mean that at a height one mile above the earth there are 5×10^3 electrons per cc which is probably too large a number in general. If we then suppose that there are no electrons in the lower atmosphere up to a height h_0 and that the linear density law (13) sets in thereafter, it is easily seen that the ray-paths are straight lines in the region h_0, changing to arcs of parabolas in the region above h_0 and finally be-

coming straight lines again when the ray returns to levels below h_0. The skip distance formula corresponding to (20) is in this case

$$s=(h_0+2h')\tan\phi\,. \tag{21}$$

$h'+h_0$ is the height of the summit of the ray above the earth, which is the height of the Heaviside layer. As h_0 increases from 0 to 76 miles, $h'+h_0$ increases from 76 to 152 miles, and we pass from the electron distribution of (13) to the case of abrupt reflection. Because of the similarity of (21) and (20) all that has been said of the applicability of the reflection theory results to Case 1 applies equally well to the present case of refraction.

17. *Case 2. Electron density proportional to square of height.* In the notation of Case 1, it is assumed that

$$N=\beta y^2\,. \tag{22}$$

Proceeding exactly as in Case 1, the equation of the ray path is

$$y=(\sqrt{1-a^2}/\sqrt{\gamma})\sin(x\sqrt{\gamma}/a)\,, \tag{23}$$

which is a sine curve. The skip distance formula is

$$s=(\pi h/2)\tan\phi\,, \tag{24}$$

and the height h comes out to be 97 miles.

18. *Case 3. Electron density proportional to exp. (height).* It is assumed that

$$N=\beta\epsilon^{y} \tag{25}$$

and proceeding as before the equation of the ray-path is

$$x=\frac{a}{\sqrt{1-a^2}}\log_\epsilon\left\{\frac{2(1-a^2)-\gamma\epsilon^{y}+2\sqrt{(1-a^2)(1-\gamma\epsilon^{y}-a^2)}}{\gamma\epsilon^{y}}\right\}. \tag{26}$$

The skip distance formula is

$$s=(\tan\phi)\log_\epsilon\left\{2\epsilon^{h}-1+2\sqrt{(\epsilon^{h}-1)\epsilon^{h}}\right\}, \tag{27}$$

from which h is 149 miles. This is a special case of an exponential distribution, but possesses all the essential features of a more general type which would be described by $N=\beta e^{by}$, where b is a constant.

Since the skip distance formulas (24) and (27) are similar to (9), the reflection theory results also apply to these cases, the height of the Heaviside layer being different, of course. Furthermore, corollary cases similar to Case 1a when carried out for Cases 2 and 3 gave results exactly similar to those of Case 1a. This is so evident that the details are omitted.

19. *Case 4. Electron density proportional to square root of the height.* From the assumption that

$$N=\beta y^{1/2} \tag{28}$$

the equation of the ray-path is

$$x=(4a/\gamma^2)\sqrt{1-\gamma y^{1/2}}\left\{1+2a^2/3+(1-\gamma y^{1/2})/3\right\} . \tag{29}$$

The skip distance formula is

$$s=(8/3)h \tan \phi \cdot (3/\cos^2 \phi-1) . \tag{30}$$

It was found impossible to choose constants for the dispersion formulas such that (30) be in accord with the observed skip distances. Similar discrepancies with observation resulted from the assumption that $N=\beta y^{1/3}$ and $N=\beta y^{1/4}$.

20. *Case 4a.* In this instance we modify Case 4, just as was done in Case 1a, and assume that no electrons exist below a height h_0 and that the electron distribution of Case 4 begins there. The skip distance formula becomes

$$s=h_0 \tan \phi+(8/3)h' \tan \phi \cdot (3/\cos^2 \phi-1) . \tag{31}$$

It was found that this formula was at variance with the observed skip distances as long as the second term was important, which occurred when h_0 was small. As h_0 becomes larger the second term becomes of less effect, and we appoach the sharp reflection case and better agreement with observation.

21. In taking up the refraction cases 1, 2, and 3 in turn we have passed from an electron distribution linear with the height progressively to electron distributions for which the N, y curve becomes more and more convex to the Y axis, approaching the distribution for sharp reflection, and have arrived at heights of the Heaviside layer which became in turn nearer to 152 miles. All these have yielded the same $\lambda,2s$ curve in agreement with observation, i. e., the curve of Fig. 1, and therefore all are equally possible as far as this agreement is concerned. On the other hand, it has been shown in Case 4 that an electron distribution for which the N,y curve is concave to the Y axis led to pronounced discrepancies with the observed skip distances. This is all in comforting agreement with reasonable expectation. On general physical grounds one would expect an electron distribution whose rate of increase became greater with the height, whereas it is difficult to imagine the stable existence of a distribution whose rate of increase became less with the height. The conclusion to be derived is *that the electron density N,*

during full daylight and averaged over all the days of the year, of the atmosphere of the earth increases with the height y in such a way that the N,y curve is for the most part convex to the Y axis, and that N reaches a maximum value of the order 10^5 *for a height which is between 70 and 150 miles.*

Again, the increase of the skip distance at night which indicates an increase in h is to be expected. For, with the removal of the sun's radiation, (electromagnetic, electronic, etc.), which is probably the most potent cause of ionization in the atmosphere, recombination of the ions and electrons will occur. The electron density therefore becomes less and the radio rays must search higher altitudes before being turned back to the earth.

22. Certain details of the dispersion equations (2), (3), (5) and (6) are of interest. From all the equations at any wave-length less than $\lambda_0 = 214$ meters, μ decreases to zero and becomes imaginary as N (or C) increases. This means that a ray of this wave-length directed normally upwards passes through regions of decreasing μ (and hence moves with increasing velocity) until it reaches that electron concentration for which $\mu = 0$ and there is totally reflected (or refracted) back to the earth. *Therefore wave-lengths from about 60 to 200 meters will be totally reflected from the layer at all angles of incidence.* The different component modes of polarization will penetrate to different heights. For waves shorter than 50 meters, N can not become large enough to make μ imaginary, since the calculations fix the maximum value of N as 10^5, and hence these rays are not totally reflected at normal incidence, but at a greater angle; this of course is the essence of the fore-going skip distance theory.

For waves longer than 214 meters, μ decreases to zero and thence to imaginary values with increase of N in the cases of equations (3), (5) and (6). From Eq. (2) however, μ is always positive for these waves and increases from 1 as N grows larger. *Therefore for waves longer than 214 meters the modes of polarization corresponding to equations* (3) (5) *and* (6) *will be totally reflected from the layer at all angles of incidence, the mode of equation* (2), *however, always being refracted upward and being probably lost.* (Eq. (5) has further mathematical complexities which appear to be of no physical significance). The prediction that these waves suffer total reflection even at normal incidence should perhaps admit of direct experimental proof. For long waves, greater than 500 meters, (3) reduces approximately to $\mu^2 = 1 - C\lambda\lambda_0$ and (5) and (6) to $\mu^2 = 1 - C\lambda^2$. These are about the same for small values of C, and the latter is the refraction formula for zero magnetic field. Hence

the earth's magnetic field has little influence in the bending of the long waves, and therefore Larmor's development, which neglected the magnetic field of the earth and referred to long waves is valid throughout.

Distortion of the Received Wave

23. We must now call to mind certain well-known radio phenomena concerning the distortion of the received wave usually resulting in fading, i. e., fluctuations in intensity, of continuous wave signals and in poor modulation and fading of speech signals. Two general types of fading are differentiated, which we now recognize as attributable to quite different causes. One type, which is common to all wave-lengths is an intensity fluctuation of relatively long period, of the order of a second or more. This is usually more noticeable at nearer distances than at greater distances from transmitter, and in general the longer the wave the slower the fluctuation. The other type is a fading at high speed, the signal intensity often varying from full strength to practically zero at a low audio frequency of the order of, say, 100 oscillations per second. This appears as a change in the quality of the heterodyne note when continuous wave signals are being received and as bad distortion in the case of speech signals. The audio frequency fading characteristic applies only to certain bands of wave-lengths at certain distances from the transmitter; it is, generally speaking, less observable in the day time and at longer distances. More specifically, for waves longer than 800 meters, roughly, the high speed fading rarely occurs; in the broadcast band, 300 to 600 meters, it is noticeable only at intermediate distances, at night especially, from about 100 to 1000 miles from the transmitter. In the region of shorter wave-lengths from 60 to 120 meters the high speed fading is violent at night for distances from roughly 5 to 300 miles from the transmitter. For the wave-lengths 16 to 40 meters the audio frequency fading is found in the flicker zones at the edge of the skip regions. Every detail of these fading phenomena finds a ready explanation in terms of the refraction ideas of this paper, and although qualitative, furnishes strong confirmation of those ideas.

24. With regard to the fading at low frequency, of a few seconds in period, we adopt the view, already suggested by many others, that this is due to a distortion of the received wavefront by motions of large clouds of the refracting electron medium. On the assumption, which appears very reasonable, that the bodily motions of the electron clouds are of the same order of velocity and extent as the air movements and

currents in the lower atmosphere, one would expect low frequency fluctuations in a wave refracted through such a medium. The phenomenon is a repetition on a larger and slower scale of the twinkling of the stars or of the unsteadiness of a scene viewed over the surface of a hot road. For longer waves motions of larger electron clouds are necessary to modify the wave-front, and these on the average would be expected to be slower than in the case of smaller clouds, so that the fading would be slower. Futher, for long distances for all wave-lengths the integrated cloud movements and hence the refraction effects would be expected to average out. This is all in accord with observation.

25. The audio frequency fading is attributed to shifting interference patterns, and finds its optical analogue in the "light beats" of Airy and Righi.[19] Thus, considering the band of waves from 300 to 600 meters, which exhibit occasionally audio frequency fading at distances from 100 to 1000 miles from the transmitter, it is seen from §22 that the various polarization components of the wave, except that of Eq. (2) are totally reflected from the layer at all angles of incidence. Therefore, in this instance any receiver, no matter where situated, may expect to receive in general four possible rays, the ground wave and the three overhead waves of Eqs. (3), (5) and (6) which travel to the receiver by different paths. In the first 100 miles from the transmitter the ground wave is sufficiently intense to drown out any variations contributed by the overhead components. Beyond 100 miles the intensity of ground wave for these wave-lengths becomes comparable with or less than that of the overhead waves, with the result that a complicated interference pattern of various states of polarization and intensities is formed about the receiver. Movements of the electron layer will cause this pattern to shift to and fro, thereby causing the rapid fluctuation of signal intensity. In daylight the electrons gather into low lying clouds of relatively great density gradient, so that the paths of different overhead rays are relatively close together and the interference pattern becomes broad and hazy. Its movements therefore cause little change in the signals. At night, however, the electrons are more diffuse and their density gradient is much less, so that the ray paths are more wide'y separated. The interference bands are therefore narrower and sharper and the motion of the pattern will cause rapid and violent intensity variations. At distances greater than 1500 miles the ray paths are so long that the interference pattern becomes indistinct in both day and night and the average effects on it of electron cloud movements become less. It is interesting that these

[19] Airy and Righi, Journal de Physique, **2**, 437 (1883).

considerations call for the propagation of even these relatively long waves to great distances by an overhead route.

By similar reasoning fast fluctuations would not be expected to occur for long waves at any place, because in the near distances the ground wave is strong and in the far distances the interference pattern is diffuse. In the case of the 16 to 40 meter band it is easily seen that the possibilities for sharp interference exist only on the edge of the skip zones.

26. The discussion of the wave band from 60 to 120 meters is along similar lines. Here, however, the rapid fading occurs at distances as small as 5 miles from the transmitter. This means that for these waves at this distance the over-head components reach the receiver with an intensity comparable with that of the ground wave, even after traveling 100 miles or so up into the upper atmosphere and being reflected back at nearly normal incidence! There seems to be no escape from the conclusion that the ground wave in this case dies out rapidly and that the over-head components are very perfectly reflected. Thus what has long been an exceedingly puzzling phenomenon finds an equally startling explanation, startling at least until one accepts these ideas.

27. The various components of the wave, besides interfering, also may arrive at a receiver at different times, because of the different paths which they traverse. This will have no effect on the interference patterns just discussed, if the wave trains are long, as in continuous wave signals, but will become an additional cause of distortion in the case of short wave trains, such as the modulated waves of speech signals. In order to estimate the magnitude of this we assume that the electron distribution of Case 1a is the one which actually exists for daylight conditions and take $h_0 = 30$ miles; $N = 0$ at this height. From the skip distance data and Eq. (21), $h' = 61$ miles and $h_0 + h' = 91$ miles where $N = 3.95 \times 10^5$. This gives the electron density gradient. From this and the dispersion equations (2), (3), (5) and (6) it is found that $\mu = 0$ at heights 69, 86, 78 and 64 miles, respectively. These are the heights where total reflection occurs for the respective waves, as discussed in §22. Assuming normal incidence the differences of the paths of the rays from the transmitter to the region of total reflection and back to the receiver are roughly 20 miles, or 10^{-4} seconds. The rays, moreover, pursue their respective paths with different speeds, which are slower in the longer paths. Calculation shows that this will increase the time differences of the paths by two or three times, making them, say, 3×10^{-4} seconds. This would perhaps be barely perceptible in speech signals. At night, however, the ray-path differences would be

increased roughly three times, and the time differences would be of the order of 10^{-3} seconds or more, which would cause strong distortion of the speech signals. This estimate of the time differences of the rays has depended on the electron distribution assumed for the calculation. This suggests that an experimental analysis of the distortion in signals of wave-lengths 60 to 120 meters received at short distances from the transmitter would perhaps lead to more definite information about the electron distribution.

Long Distance Transmission

27. In the light of the foregoing conclusions it is of interest to consider the character of the reception at various distances from the transmitter. No attempt to cover all details will be entered upon, but a few cases deserve remark. It is convenient to make the diagrams from the reflection theory; the conclusions from these will be the same as from a refraction theory. In Fig. 7 the curved line AL is the surface

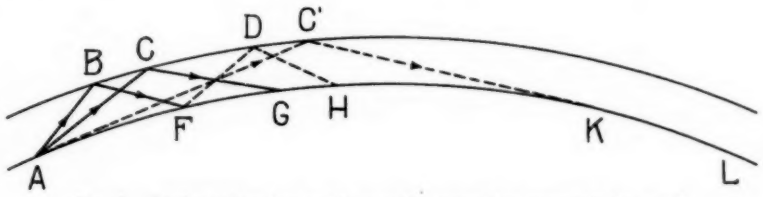

Fig. 7. Paths taken by radio rays in traveling around the earth.

of the earth and BC' the Kennelly-Heaviside layer at a height of 150 miles. Suppose that the radio rays from the transmitter A are confined to the space BAC. The upper limiting ray AB descends to F, where AF is the first skip region, is reflected back to D, down again to the earth at H, etc., continuing around by successive reflections. The lower limiting ray may be tangent to the earth as shown by AC' or may be inclined at an angle to the horizontal in the manner of AC. In the latter case if $AG<AH$, where $AH=2AF$, there exists a second smaller skip region GH. From a continuation of the drawing further skip zones are found at greater distances. These are possible, but perhaps not probable because they become successively smaller and more ill-defined.

If the bundle of transmitted rays is limited on its lower side by the tangent ray AC', which is reflected to the earth again at K, the region KL can be reached by a ray from A only after at least one ground reflection and two layer reflections (refractions). With a layer height of 150 miles AK is 2000 miles. The region FK, on the other hand, can be

reached by a ray which has experienced only one layer reflection and no ground reflection. Therefore, because the ground reflecting power may vary with the locality, one might expect possibilities of poorer signals in the region *KL* than in the region *FK*, quite apart from the difference in remoteness; or, more graphically, the poor reception at a station 5,000 miles away may be due to a forest 2500 miles away. This distinction between the regions less and greater than 2,000 miles would seem to be generally valid at all wave-lengths for which the direct ground wave is inoperative and for all the electronic distributions permissible in §§15 to 20.

The observational data relevant to these questions are none too certain, but a recent program of tests with the 25.6 meter transmitter from this station (NKF) has permitted a few conclusions. A portion of the program involved the reception of the signals at every hour of a 24-hour day by some forty stations scattered to 7000 miles distance. In the first place, the first daylight skip zone for 25.6 meters was found to be between 500 and 600 miles, which is in excellent agreement with Fig. 1. Secondly, no secondary skip zone, as *GH*, Fig. 7, appeared; the region from 700 to 1200 miles in daylight being unmistakably one of good signals. This meant merely that the lower transmitted rays were probably near to tangency with the earth, as AC', Fig. 7. In this connection it might be possible to elevate the ray AC' until the second skip zone was produced, by properly loading and exciting the transmitting antenna.[20] Thirdly, the signals in the region from 2000 to 3000 miles appeared more uncertain than in the region within the 2000 mile mark. The observations referred mainly to over-land waves and it would be of interest to repeat them with over-sea waves.

In general, for the shorter waves observations by many receiving stations in the United States indicate better signal reception in the region extending from the first skip zone to 2000 miles than in the region between 2000 and 4000 miles where at least one earth reflection is involved. At greater distances, however, from 5000 to 10,000 miles the short wave signals are very reliable, much more so than in the 2000 to 4000 mile zone. This is to be expected because, with increase of distance, there are a greater number of possible ray-paths connecting the transmitter and receiver, so that a local disturbance, such as a poor earth reflection, etc., of any one ray will have small influence on the signal. One might expect the inverse distance law of signal intensity to hold approximately in this region for the short waves.

[20] Van der Pol, Proc. Phys. Soc. London **29**, 269 (1916-1917).

At the antipodes of the earth there is a concentration of ray paths and a corresponding increase in signal strength. This has been frequently observed.

For radio communication over longer distances, of the interplanetary order, waves shorter than 40 meters would appear to be best able to pierce our own electron atmosphere as well as that of another planet. The circularly polarized long wave of Eq. (2) is of speculative utility, depending as it does on the intensity of magnetization of the electron atmosphere. Venturing even further into the realm of conjecture, the course of a ray proceeding in interplanetary space would be influenced by the electrons distributed from the sun. If this distribution were impartial in all directions, the electron density increases toward the sun, and the radio ray would be diverted towards the sun. It might pass beyond the influence of the sun after a small deflection, or it might spiral towards the sun until it reached that electron density requisite for total reflection, whereupon it would pursue an enlarging spiral until free again.

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THE STRUCTURE OF THE HYDROGEN MOLECULE ION*

By H. C. Urey

Abstract

The energies and dimensions of the hydrogen molecule ion for steady states in which the electron moves in orbits lying in the median plane between the two nuclei and perpendicular to the line joining them have been calculated. The steady states in which the electron moves in a straight line perpendicular to and through the mid point of the line joining the nuclei have energies which are given by the formula

$$W=-1.2300\ R_\infty h(1/n^{*2}),\quad n^*=1,\ 2,\ 3.....$$

The normal state for which $n^*=1$, has the energy $W=-1.2300\ R_\infty h$, which agrees with the value calculated previously by Langmuir. Tables are given of the energy of each of the other steady states in which the electron moves in the median plane with angular momentum about the line joining the nuclei. These steady states are dynamically unstable on the basis of classical mechanics with respect to a displacement in the direction of the line joining the nuclei. It is found that Olson and Glockler's work on the ionizing potentials of hydrogen can be interpreted in such a way as to be consistent with these calculations. Five of their critical potentials agree with the calculated values for dissociation of the ion and resonance of the atom to the 3, 4, 5, 6, and 7th quantum states. The absence of the resonance to the second quantum state is consistent with the theory and the interpretation of their data. Two of their critical potentials agree with the theoretical values for resonance to the 3rd and 4th vibration quantum states of the ion and another to resonance to the 3rd circular orbit of the median plane. Their highest critical potential agrees with the calculated value for complete dissociation of the ion into two protons and an electron. The interpretation of the work of these men, which leads to the agreement with the theory, also gives a means of calculating a maximum value for the *heat of dissociation of the hydrogen molecule*, of 102, 500 cal. (4.43 volts), which agrees well with values secured by direct experimental methods. It is also shown that the dimensions of the model agree with values to be expected from a consideration of the moments of inertia of the hydrogen molecule in its excited states. The *calculated moment of inertia* of H^+_2 in its normal state is 2.60×10^{-41} g. cm^2.

1. Introduction

In his original papers on the structure of atoms and molecules, Bohr[1] considered a model for the hydrogen molecule ion consisting of two hydrogen nuclei and one electron moving in a circular orbit in the

* A brief report of the work reported in this paper was presented before the National Academy of Sciences at Washington, D.C. on April 27, 1925, and appeared in the Proceedings of the National Academy of Sciences, Vol. 11, 618-621 (1925).

[1] N. Bohr, Phil. Mag. **26**, 857 (1913).

median plane between the two nuclei. The energy and dimensions of the model are fixed by the conditions that the angular momentum about the line joining the nuclei is an integral multiple of $h/2\pi$ and that the repulsive force of the nuclei on each other is equal to the component of the attractive force between the electron and one nucleus in the direction of the line joining the nuclei. He showed that this model would be dynamically unstable with respect to a blow in the direction of a line joining the nuclei or a small displacement from the median plane and therefore considered that this model was improbable. The energy and dimensions of the model as functions of the quantum number, derived by elementary methods, are given by Sommerfeld.[2]

In 1922 Pauli[3] and Niessen[4] working independently again took up this problem and considered all the various types of orbits to be expected. The dynamically stable orbit was found to have the energy, $W=-0.5175\ Rh$, where R is the Rydberg constant. This corresponds to an ionizing potential of 7.00 volts for the ion and would lead to an ionizing potential of about 23 volts for the hydrogen molecule. Horton and Davies[5] by the method of electron bombardment subsequently found an inelastic collision at 22.8 volts, which they attributed to the ionization of the hydrogen molecule. Smyth[6] showed, however, by the positive ray method for ionizing potentials that no ions are produced in the neighborhood of this point. It seems therefore that the state calculated by Pauli and Niessen is not the normal state of the hydrogen molecule ion.

Pauli and Niessen did not calculate the energies of the states having the orbits in the median plane since, as they showed, these orbits are unstable with respect to the small displacement from this plane. Such a displacement would cause the electron to move in an orbit which would not lie in the immediate neighborhood of the original orbit. They emphasize the necessity of considering this condition of dynamic stability and their arguments would be entirely valid if atomic systems obeyed in all details the laws of classical mechanics. The work of several authors[7] on the helium atom is convincing evidence that this

[2] A. Sommerfeld, Atomic Structure and Spectral Lines, 3rd ed. Appendix 14.
[3] W. Pauli, Jr., Ann. d. Physik **68,** 177 (1922).
[4] K. F. Niessen, Dissertation, Utrecht (1922); Ann. d. Physik **70,** 129 (1923).
[5] F. Horton and A. C. Davies, Phil. Mag. **46,** 872 (1923).
[6] H. D. Smyth, Proc. Roy. Soc. **105A,** 116 (1923).
[7] J. H. van Vleck, Phil. Mag. **44,** 842 (1922);
H. A. Kramers, Zeits. f. Physik **13,** 312 (1923);
M. Born and W. Heisenberg, Zeits. f. Physik **16,** 229 (1923);
A. Sommerfeld, Atombau und Spectrallienien, 4th ed. p. 197 (1924).

is not the case. If then we must discard the laws of classical mechanics for the complete description of the helium atom and atoms of higher atomic number and yet are able to use them for the description of the hydrogen and ionized helium atoms, it seems possible that some simple modification might make it possible to describe the hydrogen molecule ion. The stability of atoms and molecules in general, when considered from the standpoint of classical mechanics, is very surprising and rather suggests that this condition of dynamic stability should be the first to be modified. If these unstable orbits of the median plane of the hydrogen molecule ion exist, it probably means that there is no natural means of displacing the electron from its quantum orbits except by removing it to another quantum orbit, and that classical mechanics and the quantum conditions must be modified in such a way that these orbits are stable. The calculation of these orbits, as suggested here, can be regarded only as an incomplete description of this system.

The application of quantum mechanics according to the original ideas of Bohr[1] and the quantum conditions of Wilson[8] and Sommerfeld[9] to the hydrogen and ionized helium atoms, both unperturbed by external fields and perturbed by homogeneous electric and magnetic fields, has been so successful, that it doubtless gives a close approximation to the truth. If then it is possible to describe the hydrogen molecule ion, using these same ideas and making only the modification with regard to the question of dynamic stability, it might serve as a stepping stone for the final solution of atomic mechanics.

Langmuir[10] suggested a model for the hydrogen molecule ion in which the electron is assumed to move in a straight line in the median plane perpendicular to and passing through the line joining the nuclei. He calculated the energy for the normal state of the ion and found it to be $-1.229\ Rh$. In the spring of 1925, the author without knowledge of Langmuir's previous work calculated the energy of this same model and found it to be $-1.2300\ Rh$ which is in excellent agreement with Langmuir's calculations and serves as an independent check for this quantity. Langmuir did not publish the detailed account of his calculation to my knowledge and therefore the details of my calculation will be given in this paper. The quantum conditions are applied according to the statement by Wilson[8] and Sommerfeld,[9] and the mean value of the component of the force of attraction between the electron and one nucleus in the direction of the line joining the nuclei is set equal to the

[8] W. Wilson, Phil. Mag. **29**, 795 (1915).
[9] A. Sommerfeld, Ann. d. Physik **51**, 1 (1916).
[10] I. Langmuir, Science **52**, 436 (1920).

force of repulsion between the two nuclei. The calculated values for the resonance and ionizing potentials agree with nine critical potentials observed by Olson and Glockler[11] within a few hundredths of a volt in all cases and suggest a consistent explanation of their results which is somewhat different from that given by the authors themselves. The interpretation of their work leads to a value for the heat of dissociation of hydrogen into its atoms which agrees well with determinations of this quantity by other methods.

The application of quantum mechanics to the hydrogen molecule ion with special reference to the orbits of the median plane is presented in paragraph 2. For further detail the reader should refer to the very complete work of either Pauli[3] or Niessen.[4] In paragraph 3 the experimental work on the ionizing potentials is reviewed and the agreement with the calculations is discussed. Paragraph 4 is a discussion of the possible structure of the hydrogen molecule and the relationship between the band spectrum of the hydrogen molecule and the structure of the hydrogen molecule ion.

2. The Application of Quantum Mechanics to the Hydrogen Molecule Ion with special Reference to the Orbits of the Median Plane

Charlier[12] has given a complete discussion of the dynamical problem of two fixed centers of force acting on a third with forces varying as the inverse square of the distance and Pauli and Niessen have discussed in detail the application of the quantum theory to this problem for the case of the hydrogen molecule ion. It is therefore unnecessary to repeat in detail their derivation of the formulas involved and only that necessary for the special class of orbits considered here will be repeated. The symbols used by these two authors differed. In this paper the symbols and general method used will be those of Pauli.

For the first approximation the nuclei may be regarded as having infinite mass and therefore as fixed. The energy and dimensions of the system will be determined by two sets of conditions, the quantum conditions applied to the motion of the electron and the condition that the mean force acting on the nuclei in the direction of the line joining them shall be equal to zero. The latter condition fixes the relative proportions of the model. The quantum conditions fix the absolute values.

[11] A. R. Olson and G. Glockler, Proc. Nat. Acad. Sci. **9**, 122 (1923).

[12] C. L. Charlier, Die Mechanik des Himmels, vol. 1, Chap. III, p. 122, Leipzig (1902).

The separation of variables for the problem of two fixed centers of force can be secured in elliptical co-ordinates. For the special class of orbits lying in the median plane the separation can be secured in plane polar co-ordinates in this plane with the origin at the point of intersection of the plane and the line joining the nuclei. Since these co-ordinates are somewhat more easily thought of, the dynamical equations can be set up in these co-ordinates. For purposes of integration it is convenient to change to the elliptical co-ordinates. The kinetic energy in polar co-ordinates is

$$T=\tfrac{1}{2}m(\dot{r}^2+r^2\dot{\phi}^2)\ ,$$

and the potential energy

$$V=e^2/2c-2e^2/\sqrt{r^2+c^2}\ ,$$

c being one half the distance between the nuclei. The Hamiltonian function is secured by substituting the momenta conjugate to r and φ for the $\dot{r}$ and $\dot{\varphi}$ in the kinetic energy and adding the potential energy.

$$H=\frac{p_r^2}{2m}+\frac{p_\varphi^2}{2mr^2}+\frac{e^2}{2c}-\frac{2e^2}{\sqrt{r^2+c^2}}\ . \tag{1}$$

The variables in this equation can be separated and the quantum conditions are

$$\oint p_r dr=J_1=n_1h\ , \qquad \oint p_\varphi d\varphi=J_3=n_3h\ , \tag{2}$$

where n_1 and n_3 are integral numbers and h is Planck's constant. The condition that the mean value of the force on the nuclei in the direction of the line of nuclei shall be zero is easily shown to be

$$\overline{\frac{e^2c}{(r^2+c^2)^{3/2}}}=\frac{e^2}{4c^2}\ , \tag{3}$$

the bar over the quantity indicating that the mean value is to be taken.

In order to perform the integrations it is convenient to change the variables from r and φ to λ and φ, λ being defined by the equation

$$\lambda=\sqrt{r^2+c^2}/c.$$

If λ were defined as the ratio of the sum of the two distances from the electron to the two nuclei to the distance between the two nuclei, it would define an ellipse. It is therefore one of the elliptical co-ordinates

used by Pauli and Niessen. The change of co-ordinates can be made by a contact transformation derived from the function

$$V = p_r c\sqrt{\lambda^2-1} + p_\varphi \varphi \ .$$

The new conjugated variables are

$$\begin{aligned} r &= \frac{\partial V}{\partial p_r} = c\sqrt{\lambda^2-1} \ , & p_\lambda &= \frac{\partial V}{\partial \lambda} = p_r \frac{c\lambda}{\sqrt{\lambda^2-1}} = \frac{mc^2\lambda^2\dot{\lambda}}{\lambda^2-1} \ , \\ \varphi &= \frac{\partial V}{\partial p_\varphi} = \varphi \ , & p_\varphi &= \frac{\partial V}{\partial \varphi} = p_\varphi \ . \end{aligned} \tag{4}$$

and the Hamiltonian function expressed in these co-ordinates is

$$H = \frac{\lambda^2-1}{2mc^2\lambda^2} p_\lambda^2 + \frac{p_\varphi^2}{2mc^2(\lambda^2-1)} - \frac{2e^2}{c\lambda} + \frac{e^2}{2c} \ , \tag{5}$$

and this is equal to the total energy W, which is constant. The phase integrals (2) become

$$J_1 = \sqrt{a_1} \oint \frac{\sqrt{F(\lambda)}}{\lambda^2-1} d\lambda \ , \qquad J_3 = \oint p_\varphi d\varphi = 2\pi a_3 \ , \tag{6}$$

where the following substitutions have been made:

$$F(\lambda) = -\lambda^4 + B\lambda^3 + (1-A)\lambda^2 - B\lambda \ , \tag{7}$$

$$a_1 = mce^2 - 2mc^2 W \ , \qquad A = \frac{a_3^2}{a_1} \ , \qquad B = \frac{4e^2 mc}{a_1} \ . \tag{8}$$

The condition of Eq. (3) in the new co-ordinates is

$$\overline{\frac{1}{\lambda^3}} = \mathscr{S}(1/\lambda^3)dt / \mathscr{S} dt = 1/4 \ . \tag{9}$$

From Eq. (4) and the relation $p_\lambda = \sqrt{a_1}\sqrt{F(\lambda)}/(\lambda^2-1)$, we find that

$$dt = \frac{mc^2}{\sqrt{a_1}} \frac{\lambda^2 d\lambda}{\sqrt{F(\lambda)}} \ , \tag{9a}$$

and substituting this in (9), the condition for zero force acting on the nuclei in the direction of the line of nuclei becomes

$$\oint \frac{d\lambda}{\lambda\sqrt{F(\lambda)}} = \frac{1}{4} \oint \frac{\lambda^2 d\lambda}{\sqrt{F(\lambda)}} \ . \tag{10}$$

The integrals which have been indicated are elliptic integrals, which can be reduced to the standard forms by the usual change of variables.

If the roots of $F(\lambda)=0$ are $\lambda_1, \lambda_2, \lambda_3$ and λ_4, these can be arranged so that $\lambda_3<\lambda_4<\lambda_1<\lambda_2$, the limits of oscillation being λ_1 and λ_2. λ_3 can be expressed in terms of λ_1 and λ_2, thus

$$\lambda_3=-\frac{\lambda_1+\lambda_2}{1+\lambda_1\lambda_2}$$

and $\lambda_4=0$. The reduction to the normal form can be secured by changing to the variable z according to the equations

$$\lambda=\frac{\lambda_1}{1-nz^2}, \qquad n=1-\frac{\lambda_1}{\lambda_2}, \qquad k^2=\frac{\lambda_2-\lambda_1}{\lambda_2}\cdot\frac{-\lambda_3}{\lambda_1-\lambda_3}=n\frac{\lambda_3}{\lambda_3-\lambda_1}. \tag{11}$$

The integrals indicated in Eqs. (6) and (10), when expressed in terms of z, are

$$\int_{\lambda_1}^{\lambda_2}\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda = 2\lambda_1{}^3n^2\sqrt{\frac{n}{(1-n)(n-k^2)}}\int_0^1\frac{(1-z^2)(1-k^2z^2)z^2}{(1-nz^2)(\lambda_1{}^2-(1-nz^2)^2)}\frac{dz}{\sqrt{(1-z^2)(1-k^2z^2)}}, \tag{12}$$

$$\int_{\lambda_1}^{\lambda_2}\frac{d\lambda}{\lambda\sqrt{F(\lambda)}}=\frac{2}{\lambda_1{}^2}\sqrt{\frac{(1-n)(n-k^2)}{n}}\int_0^1\frac{(1-nz^2)dz}{\sqrt{(1-z^2)(1-k^2z^2)}}, \tag{13}$$

$$\int_{\lambda_1}^{\lambda_2}\frac{\lambda^2d\lambda}{\sqrt{F(\lambda)}}=2\lambda_1\sqrt{\frac{(1-n)(n-k^2)}{n}}\int_0^1\frac{dz}{(1-nz^2)^2\sqrt{(1-z^2)(1-k^2z^2)}}. \tag{14}$$

The integrals[13] (13) and (14) can be expressed in terms of the elliptic

[13] The following equations are used in securing Eq. (15):

$$\int_0^1\frac{(1-nz^2)dz}{\sqrt{(1-z^2)(1-k^2z^2)}}=\frac{n}{k^2}E-\frac{n-k^2}{k^2}K_1, \tag{15a}$$

$$\int_0^1\frac{dz}{(1-nz^2)^2\sqrt{(1-z^2)(1-k^2z^2)}}=\frac{\lambda_1{}^2k^2}{2(1-n)(n-k^2)}\Pi(n\ ,\ k)+\frac{n}{2(1-n)(n-k^2)}E-\frac{1}{2(1-n)}K_1,$$

$$\lambda_1=\frac{\sqrt{(2k^2-n)(n-2)+k^2}}{K}.$$

integrals of the first, second and third kinds and when so expressed and substituted in Eq. (10), this reduces to

$$\frac{\lambda_1^5}{8}\frac{k^2}{(1-n)(n-k^2)}\Pi(n,k)-\left(\frac{n}{k^2}E-\frac{n-k^2}{k^2}K\right)\left(1-\frac{k^2\lambda_1^3}{8(n-k^2)(1-n)}\right)=0, \tag{15}$$

where

$$K=\int_0^1\frac{dz}{\sqrt{(1-z^2)(1-k^2z^2)}}, \qquad E=\int_0^1\sqrt{\frac{1-k^2z^2}{1-z^2}}dz$$

and

$$\Pi(n,k)=\int_0^1\frac{dz}{(1-nz^2)\sqrt{(1-z^2)(1-k^2z^2)}}.$$

The fraction

$$\frac{(1-z^2)(1-k^2z^2)z^2}{(1-nz^2)^2(\lambda_1^2-(1-nz^2)^2)}$$

in Eq. (12) can be broken up into simple fractions with the denominators $(1-nz^2)^2$, $1-nz^2$, $\lambda_1-(1-nz^2)$, and $\lambda_1+(1-nz^2)$. Then

$$\int_{\lambda_1}^{\lambda_2}\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda=\lambda_1^3\sqrt{\frac{n}{(1-n)(n-k^2)}}\left\{-\int_0^1\frac{2(n-k^2)(1-n)dz}{\lambda_1^2n(1-nz^2)\sqrt{(1-z^2)(1-k^2z^2)}}\right.$$

$$+\int_0^1\frac{2k^2dz}{n(1-nz^2)\sqrt{(1-z^2)(1-k^2z^2)}}+\left(\frac{3k^2}{n}-(1+k^2)-\frac{(n-k^2)(1-n)}{\lambda_1^2n}\right)$$

$$\frac{1}{\lambda_1}\left[\int_0^1\frac{dz}{(\lambda_1-1+nz^2)\sqrt{(1-z^2)(1-k^2z^2)}}\right.$$

$$\left.\left.+\int_0^1\frac{dz}{(\lambda_1+1-nz^2)\sqrt{(1-z^2)(1-k^2z^2)}}\right]\right\}$$

Using the Eq. (15a) and the above equation, we get

$$\int_{\lambda_1}^{\lambda_2}\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda=\lambda_1^3\sqrt{\frac{n}{(1-n)(n-k^2)}}\left\{\frac{k^2}{n}\Pi(n,k)-\frac{1}{\lambda_1^2}E+\frac{n-k^2}{\lambda_1^2n}K\right. \tag{16}$$

$$+\left(\frac{3k^2}{n}-(1+k^2)-\frac{(n-k^2)(1-n)}{\lambda_1^2n}\right)$$

$$\left.\times\frac{1}{\lambda_1}\left[\frac{1}{\lambda_1-1}\Pi(n',k+\frac{1}{\lambda_1+1}\Pi(n'',k)\right]\right\},$$

where

$$n' = -\frac{n}{\lambda_1 - 1}, \text{ and } n'' = \frac{n}{\lambda_1 + 1}.^{14}$$

The limits of integration to be used. The systems which we are considering have a limiting degeneracy[15] since the electron moves in only one or two dimensions and therefore has only one or two frequencies in its motion. For the orbits in which the electron has angular momentum about the line of nuclei, the equation $F(\lambda) = 0$ has two roots which lie between $+1$ and $+\infty$. At these two points the momentum p_λ becomes zero; it is finite at all intermediate points and the variables λ and φ do not change rapidly with the time at any point between these two limits. The phase integral is to be extended from λ_1 to λ_2 and back to λ_1, or in polar co-ordinates from r_{min} to r_{max} and back to r_{min}. These limits are similar to those used for the precessing elliptic orbits of hydrogen and are those used by Niessen in calculating orbits which do not lie in the median plane. The general character of such an orbit is shown in Fig. 1a illustrating the appearance of these orbits when viewed in the direction of the line of nuclei. The circles show the limits of oscillation, λ_1 being equivalent to r_{min} and λ_2 to r_{max}.

As the angular momentum approaches zero, these orbits approach the vibration type of orbit. The root λ_1 of $F(\lambda) = 0$ becomes equal to 1, i.e. r_{min} becomes equal to zero and this does not represent a limit of libration. The system is similar in every way to the inharmonic oscillator. For this special type of orbit, it is necessary to use rectangular co-ordinates for determining the limits of integration. The p_λ is not equal to zero at $\lambda = 1$ or r_{min} equal to 0. It therefore does not represent a limit of oscillation and the phase integral must be extended from x_1 of Fig. 1b to x_2 and back to x_1, i.e. from r_{max} to r_{max} and back to r_{max}. In terms of λ this is four times the integral from λ_1 to λ_2. The limits chosen are similar in every way to those commonly used for the inhar-

[14] The formulas for expressing the complete elliptic integrals of the third kind occurring in this equation in terms of the complete and incomplete elliptic integrals of the first and second kinds are for $\Pi(n, k)$ and $\Pi(n'', k)$, in which $1 > (n \text{ or } n'') > k^2 > 0$,

$$\Pi(n,k) = \sqrt{\frac{n}{(1-n)(n-k^2)}}\left\{E(k', \beta)\, K(k) - F(k', \beta)[K(k) - E(k)]\right\},$$

where $\sin^2 \beta = \frac{n-k^2}{n(1-k^2)}$, and $k'^2 = 1-k^2$, n'' being substituted for n throughout for $\Pi(n'', k)$, and for $\Pi(n', k)$, where $-\infty < n' < 0 < k^2 < 1$,

$$\Pi(n', k) = \sqrt{\frac{n'}{(1-n)(n'-k^2)}}\left\{\frac{\pi}{2} - E(k', \beta)\, K(k) + F(k', \beta)[K(k) - E(k)]\right\} + \frac{1}{1-n'}K(k),$$

where $\sin^2 \beta = 1/1 - n'$.

monic oscillator. It is easily seen that from the standpoint of the limits chosen for the orbits having angular momentum about the line of nuclei in the last paragraph, the orbits and steady states calculated using the limits of the phase integral chosen here are to be regarded as half quantum states.

Due to the difference in the limits over which the phase integrals are extended, as well as the greater simplicity of the equations for the vibration quantum states, it is convenient to discuss the vibration states and the states having angular momentum about the line of nuclei separately.

The vibration orbits. If the angular momentum about the line of nuclei is zero, $A=0$ and $F(\lambda)=-\lambda^4+B\lambda^3+\lambda^2-B\lambda$. The equation $F(\lambda)=0$ can be solved and has the roots

$$\lambda_1=1\ , \qquad \lambda_2=B\ , \qquad \lambda_3=-1\ , \qquad \lambda_4=0\ .$$

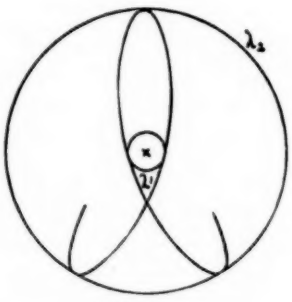

Fig. 1a

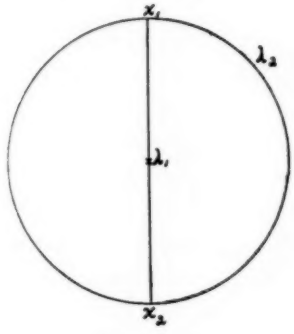

Fig. 1b

The change of variables by Eq. (11) then becomes

$$\lambda=1/(1-nz^2)\ , \qquad n=1-1/B\ , \qquad k^2=n/2\ ,$$

and Eq. (16) reduces to the simple form

$$\int_1^B \frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda=\tfrac{1}{2}\sqrt{2B}\,(\Pi(n\ ,k)-2E+K)\ .$$

Since this is 1/4 of the phase integral from x_1 to x_2 and back to x_1 the phase integral[16] J^* is

$$J^*=\sqrt{a_1}\oint\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda=2\sqrt{2Ba_1}\,(\Pi(n\ ,k)-2E+K)\ . \qquad (17)$$

[15] See M. Born, Vorlesungen über Atommechanik, Julius Springer (1925), Chap. 4, § 46.

[16] The asterisk will be used to designate the phase integrals and quantum numbers for which the limits of oscillation are x_1 and x_2 of Fig. 1b.

The condition for zero mean force acting on the nuclei in the line of nuclei from Eq. (15) becomes

$$\frac{B}{8}\Pi(n\ ,\ k)-(1-B/8)(2E-K)=0\ . \tag{18}$$

Since $a_1B=4\ mce$,[2] Eq. (17) gives for c/a

$$\frac{c}{a}=n^{*2}\frac{\pi^2}{8(\Pi(n\ ,\ k)-2E+K)^2}\ , \tag{19}$$

where a is the radius of the first quantum orbit of the hydrogen atom and $\Pi(n, k)$, E, and K satisfy Eq. (18). From Eqs. (19) and (8) the energy is found to be

$$W=-\frac{R_\infty h}{n^{*2}}\ \frac{8(\Pi(n\ ,\ k)-2E+K)^2}{\pi^2}\left(\frac{4}{B}-1\right)\ . \tag{20}$$

The Eqs. (19) and (20) give the distance between the nuclei and the energy as functions of B, which is the ratio of the maximum distance between the electron and one nucleus and half the distance between the nuclei. The solution of (19) or (20) and Eq. (27) simultaneously would give the distance between the nuclei or the energy, respectively, as a function of the quantum number and natural constants. The analytical solution of these simultaneous equations would be very difficult or impossible and it is therefore necessary to solve the equations by trial.

By trial a value of B has been found with satisfies Eq. (17). The values of K, E and $\Pi(n, K)$, which are functions of B, are then known and can be substituted in Eqs. (19) and (20). The results of the calculations are: $B=2.4297$, $K=1.71056$, $E=1.44795$, $\Pi(n, K)=2.7175$, and $c/a=0.5255\ n^{*2}$, $W=-R_\infty h\ 1.2300\ 1/n^{*2}$, and $\omega/\omega_0=(1/\omega_0)(\partial W/\partial J^*)=1.2300\ 1/n^{*3}$. In the last expression ω is the frequency of vibration of the electron in the hydrogen molecule ion and ω_0 is the frequency of revolution of the electron in the first quantum orbit of the hydrogen atom. The motion of the nuclei has been neglected, but the difference in energy due to the motion of the nuclei in the same direction as that in which the electron moves can be included in the formulae by using R_{H_2} instead of R_∞ in the formula given. This still neglects the effect of the motion of the nuclei in the direction of the line of nuclei. The calculation of B is believed to be accurate to about ± 0.0001. The value secured for the energy ($W=-1.2300\ R_\infty h$) agrees well with Langmuir's result ($W=-1.229\ Rh$) as noted above.

The orbits of the median plane having angular momentum about the line of nuclei. For these orbits the phase integral is extended from

λ_1 to λ_2 and back to λ_1 and therefore the integral given in Eq. (16) must be multiplied by 2 in order to extend this integral over a complete cycle of the motion. For this case

$$F(\lambda) = -\lambda^4 + B\lambda^3 + (1-A)\lambda^2 + B\lambda \ .$$

If we divide the Eq. (6)

$$J_1 = \sqrt{a_1} \oint \frac{\sqrt{F(\lambda)}}{\lambda^2 - 1} d\lambda$$

by

$$J_3 = 2\pi \sqrt{A a_1}$$

from Eqs. (6) and (8), we get

$$J_1/J_3 = \frac{1}{2\pi\sqrt{A}} \oint \frac{\sqrt{F(\lambda)}}{\lambda^2 - 1} d\lambda \ , \tag{21}$$

the latter integral being expressed in terms of the complete elliptic integrals by (16). The condition that the force acting on the nuclei in the direction of the line of nuclei shall be zero is given by Eq. (15). These two simultaneous equations have been solved by trial, a value of λ_1 first being chosen and then by trial a value for λ_2 found which would satisfy Eq. (15). In this way a number of pairs of such values of λ_1 and λ_2 were found and the ratio J_1/J_3 was calculated from Eq. (21) for these pairs of values of λ_1 and λ_2. From the equation

$$-\lambda^4 + B\lambda^3 + (1-A)\lambda^2 - B\lambda = (\lambda - \lambda_1)(\lambda - \lambda_2)(\lambda - \lambda_3)(\lambda - \lambda_4)$$

expressions for A and B in terms of λ_1 and λ_2 can be derived and these are

$$A = \frac{(\lambda_1^2 - 1)(\lambda_2^2 - 1)}{1 + \lambda_1\lambda_2} \ , \qquad B = \frac{(\lambda_1 + \lambda_2)\lambda_1\lambda_2}{1 + \lambda_1\lambda_2} \ .$$

By eliminating a_1 from the expressions for A and B of Eq. (8), c can be secured as a function of A and B, and by eliminating a_1 and c from the three expressions of Eq. (8) and substituting for a_3 from Eq. (6) the energy can be given as a function of A and B, and these are respectively

$$c/a = \frac{B}{4A} n_3^2$$

$$W = -\frac{1}{n_3^2} \frac{4A}{B} \left(\frac{4}{B} - 1 \right) Rh$$

The quantities $4A/B\ (4/B-1)$ and $4A/B$ were plotted against the ratio n_1/n_3 for the region in which n_1/n_3 is small and against n_3/n_1 in the region in which this is a small quantity. Smooth curves were drawn through the points and the values of $4A/B\ (4/B-1)$ and $4A/B$ for the values of n_1/n_3, which are the ratios of integral numbers, were read from the curves. The values of $4A/B\ (4/B-1)$ and $B/4A$ so secured are given in Table Ia.

TABLE Ia

n_1/n_3	$\frac{4A}{B}(\frac{4}{B}-1)$	$B/4A$	n_3
1	0.130	5.10	1
2	0.048	13.5	1
3	0.025	26.	1
4	0.015	42.	1
5	0.011	60.	1
1/2	0.280	2.44	2
3/2	0.074	8.85	2
5/2	0.034	19.2	2
1/3	0.382	1.82	3
2/3	0.209	3.22	3
4/3	0.088	7.50	3
5/3	0.064	10.3	3
1/4	0.445	1.58	4
3/4	0.183	3.65	4
5/4	0.096	6.85	4
1/5	0.489	1.45	5
2/5	0.337	2.04	5
3/5	0.235	2.90	5
4/5	0.170	3.92	5

In Table Ib are listed the values of $-W/Rh$ for the orbits of the median plane for values of n_1 and n_3 from 1 to 5. The numbers given in the first column are those of the even values of n^* only since only these numbers are comparable to the other quantities in the table due to the difference in the limits over which the phase integral is extended.

TABLE Ib

n_1 $n_3\rightarrow$ ↓	0	1	2	3	4	5
0		.8777	.2194	.0975	.0549	.0351
1	.3075($n^*=2$)	.130	.070	.0424	.028	.020
2	.0769($n^*=4$)	.048	.032	.0232	.0175	.0135
3	.0342($n^*=6$)	.025	.0185	.0144	.0114	.0094
4	.0192($n^*=8$)	.015	.0120	.0098	.0081	.0068
5	.0123($n^*=10$)	.011	.0085	.0071	.0060	.0052

3. COMPARISON WITH EXPERIMENT

The data on the ionizing and resonance potentials of molecular hydrogen are very discordant both with regard to the numerical values reported and the interpretation of these values. The ionizing potentials reported in the literature vary from approximately 11 volts to 16.68 volts, with rather consistent agreement between a number of observers

for the potentials[17] 11, 13.5 and 16.0 volts. It is very difficult to explain the ionization at 11 volts. That at 13.5 is usually attributed to atomic hydrogen which has diffused from the region of the hot filament to the point where the inelastic collisions take place. The third potential at 16 volts is usually assumed to be the ionizing potential of the molecule or the dissociation of the molecule and ionization of one of the atoms. The latter assumption gives about 2.5 volts for the dissociation potential of the molecule and this does not agree with the values secured by other methods. The agreement between the different authors is rather rough and the results of Olson and Glockler[11] are at variance apparently with the work of all other authors. The wide differences secured by different observers indicates that the method of inelastic collisions possibly gives only approximate values for the energy changes in resonance, dissociation, and ionization of molecules.

Olson and Glockler have measured, apparently with great accuracy, nine critical potentials of hydrogen between 14.84 and 16.68 volts, the latter potential having been duplicated in eight runs with a maximum variation of .11 volt. Six of these potentials can be represented by the formula

$$v = 3.16 + 13.52(1 - 1/n^2), \qquad n = 3, 4, 5, 6, 7 \text{ and } \infty \quad \cdots$$

As 13.52 is the ionizing potential of the hydrogen atom these authors assumed that these critical potentials were due to dissociation plus resonance of one atom, the dissociation potential being 3.16 volts. Resonance to the second quantum state of the atom was not observed and no explanation of this was given nor has any satisfactory explanation of this unexpected result been found since their paper was published. The remaining three potentials were assumed to be resonance potentials of the molecule. Two of these potentials can be represented by the formula

$$v = 16.68(1 - 1/n^2), \qquad n = 3, \text{ and } 4, \quad \cdots\cdots$$

and if $n = \infty$ is substituted in this formula it gives the same potential as that for $n = \infty$ in the preceding equation. The constant in this equation is the highest potential observed. This relationship was pointed out to me by Dr. A. R. Olson in 1923 at the time their paper was published. It is immediately evident that if these two empirical relations are true, then not only the differences in the potentials observed by Olson and Glockler, but also the absolute magnitude of

[17] See Bull. Nat. Res. Council, vol. 9, Part 1, No. 48, Critical Potentials by K. T. Compton and F. L. Mohler.

these potentials must be correct, for if a constant is added to the first equation, then the potential secured by setting $n = \infty$ in this equation will no longer give the constant to be used in the second equation. The latter must then be written in the form

$$V = 16.68\,(1 - 1/n^2) + \text{constant}$$

and the simplicity of Olson and Glockler's equations is lost.

No difference can be seen in the one curve published by Olson and Glockler between breaks in the curve corresponding to resonance of the molecule and those corresponding to dissociation and resonance of the atom. If these critical potentials represented by the former equation were also due to resonance without dissociation, this would be in exact accord with the work of Glitscher[18] on the many lined spectrum of hydrogen. His work indicates that there are steady states of some emitter of the many lined spectrum which differ from each other by the same amounts as the steady states of the hydrogen atom.

The very close agreement between the results of these observers and the potentials predicted from the theory of the hydrogen molecule ion is quite remarkable and if it is possible to interpret their critical potentials as being due to the hydrogen molecule ion instead of the hydrogen molecule, it indicates that a very high precision has been secured by these authors. For dissociation of the ion and resonance of the atom the potentials predicted from theory can be represented by the formula

$$v = 3.12 + 13.53(1 - 1/n^2),\ n = 2, 3, \cdots\cdots\cdots$$

and the theoretical formula for the resonance potentials of the hydrogen molecule ion (vibration quantum states only) is

$$v = 16.65(1 - 1/n^{*2}),\ n^* = 2, 3, \cdots\cdots\cdots\cdots$$

It is necessary, however, to interpret the experimental results in quite a different way from that given by the authors themselves. The calculated and observed potentials together with the interpretation given by Olson and Glockler and that given here are shown in Table II. The numbers in parenthesis refer to the quantum numbers of the steady states. The first number given in parenthesis after the hydrogen molecule ion is n_1, the quantum number conjugate to the λ co-ordinate, the second is n_2, the number conjugate to the μ co-ordinate of Pauli which is always zero for the orbits of the median plane, and the third is the n_3, the quantum number conjugate to the φ co-ordinate. The

[18] K. Glitscher, Sitzungsber. der Bayer. Akad. 1916, p. 125, See A. Sommerfeld, Atombau und Spectrallinien, 4th ed. pp. 92, 93, Friedr. Vieweg and Sohn (1924).

critical potential at 15.35 volts has been shown as resonance to the third circular orbit level. It seems to fit this transition better than any other calculated, but since only this one resonance out of all the possible rotation orbit levels appears in the experimental data, some other explanation may be possible. It may be also that the critical potentials given as dissociation and resonance of the atom are really resonance potentials as suggested above. No energy levels of the hydrogen molecule ion which have been calculated either by Niessen or by me give this simple relation, i.e. differences in energy levels equal to the differences in energy levels of the hydrogen atom. Since the mechanics which has been used is admitted to be incomplete, the possibility that these are resonance potentials of the ion is not excluded. Such a relationship is more likely to be characteristic of the hydrogen molecule ion than of either the hydrogen molecule or the triatomic hydrogen molecule or its ion, because the relatively simple structure of the hydrogen molecule ion would lead us to expect simpler relationships between the steady states.

TABLE II

Resonance potentials of the hydrogen molecule ion

Reaction (Olson and Glockler)	Reaction (Urey)	Potentials obs.	Potentials calc.
$H_2=H(1)+H^++e$	$H_2^+(1^*,0,0)=H^++H^++e$	16.68	16.65
$H_2=H(1)+H(7)$	$H_2^+(1^*,0,0)=H^++H(7)$	16.41	16.37
$H_2=H(1)+H(6)$	$H_2^+(1^*,0,0)=H^++H(6)$	16.33	16.28
$H_2=H(1)+H(5)$	$H_2^+(1^*,0,0)=H^++H(5)$	16.11	16.11
$H_2=H(1)+H(4)$	$H_2^+(1^*,0,0)=H^++H(4)$	15.84	15.80
$H_2=H_2(r)$	$H_2^+(1^*,0,0)=H_2^+(4^*,0,0)$	15.62	15.61
$H_2=H_2(r)$	$?H_2^+(1^*,0,0)=H_2^+(0,0,3)$	15.35	15.33
$H_2=H(1)+H(3)$	$H_2^+(1^*,0,0)=H^++H(3)$	15.12	15.15
$H_2=H_2(r)$	$H_2^+(1^*,0,0)=H_2^+(3^*,0,0)$	14.84	14.80
.....	$H_2^+(1^*,0,0)=H^++H(2)$	.....	13.27
.....	$H_2^+(1^*,0,0)=H_2^+(2^*,0,0)$	.....	12.49

The apparatus of Olson and Glockler is adapted for the detection of resonance potentials and not ionization potentials. Their lowest potential is 14.84 volts and it seems very probable that this is greater than the first resonance potential of the hydrogen molecule. Other observers have reported critical potentials as low as 10 volts. For some reason these do not appear in Olson and Glockler's work nor do they observe the potential corresponding to dissociation and resonance of the atom to the second quantum orbit for which the calculated value is 13.27 volts (See table II). In a previous note it was assumed that the current measured by their electrometer was due to ions, no current would be observed until the H_2^+ ion was produced by an electron of velocity between 13.27 and 14.84 volts. Due to an error in their paper this

interpretation is no longer tenable.[19] It is still possible that only light emitted by the H_2^+ ion reaches the electrometer electrode, the light produced by resonance of the molecule being absorbed by the layer of hydrogen gas between the point of excitation and the detecting electrode. Though this interpretation is open to objections, the experimental fact remains that the lowest potential observed by these authors is 14.84 volts and this is probably much larger than the first resonance potential of the molecule. This point together with others appearing in their work must be decided by further experiment. For the present we assume that all potentials observed by these men are due to the hydrogen molecule ion.

This interpretation of this experimental work gives an explanation of one of its peculiarities, namely the absence of the critical potential for dissociation and resonance of the atom to the second quantum state for which the calculated value is 13.27 volts. For if the ionizing potential of the molecule is greater than this potential, no current would be observed until this point was exceeded and thus it would not be observed. This interpretation is possible quite independently of any theoretical considerations, but leads to the conclusion that the ionizing potential of the molecule lies between 13.27 and 14.84 volts, and this appears to be in disagreement with the work of other observers.

TABLE III

Run	Initial correction	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
1	2.29		15.30			15.86	16.02		16.40	16.70
2	3.18	14.75	15.09	15.34		15.79	16.19			16.68
3	.75	14.89	15.09	15.44	15.74		16.14	16.34		16.71
4	1.39		15.25		15.61	15.92	16.16	16.33		16.68
5	1.24	14.75	14.97	15.29	15.56	15.85	16.05		16.32	16.63
6	1.28		15.17	15.41	15.70	15.89	16.14	16.36	16.56	16.73
7	1.61	14.94		15.33	15.54	15.78	16.10	16.35		16.70
8	2.08	14.89	15.08	15.28	15.56	15.76			16.38	16.62
Av.		14.84	15.12	15.35	15.62	15.84	16.11	16.33	16.41	16.68
Theor.		14.80	15.15	15.33	15.61	15.80	16.11	16.28	16.37	16.65

The complete experimental data of Olson and Glockler are given in Table III. The first column gives the run number, the second the initial correction applied, and the remaining columns the observed

[19] In a conversation between Dr. Olson and the author an error was discovered in the paper of Olson and Glockler. In their Fig. 1 the accelerating and retarding potentials A_4 and R_4, which are shown between gauzes G_3 and G_4, should be placed between P and G_4 and the zero field $A_4=0$ should have been placed between G_3 and G_4. The space between G_3 and G_4 is in effect a Faraday cage. This makes the interpretation of these potentials given by the author in the Proceedings of the National Academy of Sciences, Vol. 11, 618 (1925) an impossible one.

potential plus the initial correction of column 2. The arrangement into groups *a*, *b*, *c*, etc. is the same as that given by the authors in their Table II.

The first critical potential observed varied from 14.75 to 15.30 volts. Had they regarded these as being the same critical potential, they would have concluded that the ionizing potential was about 15 volts with an experimental accuracy of $\pm .3$ volt. This would be the usual interpretation and the limits of error would have been much the same as that secured by other observers. The highest potential observed is shown in the last column. When this is regarded as the constant critical potential, it is possible to arrange the ones preceding in groups which show fair agreement among themselves. The averages of these potentials are listed in Table III. The listing of the two columns *g* and *h* separately is rather artificial, since the points on the curves were read only at .1 volt intervals, and several other changes in arranging the observed potentials might be made as for example the first potential of column *b*, but on the whole it seems difficult to rearrange the data in any better way than that given by the authors.

There is then an erratic variation of the lowest potential observed for which there seems to be no satisfactory explanation. Richardson and Tanaka[20] have pointed out a similar difficulty in their work on the ionizing potentials of hydrogen. They say, "An examination of the data leads to the conclusion that the observed oscillation of the values between 14.6 and 15.4 volts is real and not due to errors in drawing the curves. In other words, the measured potentials may have been changing by an extreme amount of 0.8 volt in the course of these experiments." This statement can be applied without change to the first potentials recorded in Table III. Due to this variation, we are not justified in taking 14.84 volts as the ionizing potential of the molecule, but only in regarding this as a maximum. Using this interpretation, it is possible to calculate a maximum value for the energy dissociation of hydrogen gas by the following equations:

$$H_2 = H_2^+ + e \quad ; 14.84 \text{ volts (experimental)}$$
$$H_2^+ = 2H^+ + e \quad ; 16.65 \text{ volts (theoretical)}$$

adding
$$H_2 = 2H^+ + 2e ; 31.49 \text{ volts}$$

and subtracting
$$2H = 2H^+ + 2e ; 27.06 \text{ volts } (= 2\,Rh)$$

$$H_2 = 2H \quad ; \; 4.43 \text{ volts } (= 102{,}500 \text{ cal.})$$

A comparison of this value with that secured by other methods is given in Table IV.

[20] O. W. Richardson and T. Tanaka, Proc. Roy. Soc. **106A**, 640 (1924).

The value calculated here is somewhat larger than the other values given in the table. If 93,000 cal. (=4.03 volts) is about the correct value for the heat of dissociation the ionizing potential of the hydrogen molecule should be about 14.3 volts. If the 13.5 volts ionizing potential observed by several authors is made to coincide with this value by adding .8 volt, then the 16 volt potential will agree with the ionizing potential calculated for the hydrogen molecule ion. This is a possible explanation of the ionizing potential data.

TABLE IV

Author	Method	Heat of dissociation
Langmuir[21] (1915)	Conduction from a hot wire	84,000 cal.
Isnardi[22] (1915)	Conduction from a hot wire	100,000 cal.
Wohl[23] (1924)	Temperature of explosions	90,000 cal.
Olson and Glockler and from this paper	Ionizing potentials	102,500 cal. (Maximum)

The interpretation of these critical potentials suggested here, requires that the first process occurring is

$$H_2 = H_2^+ + e$$

and that the H^+ ions are produced by a second collision. This is in agreement with the work of Smyth[24] on the ionizing potentials of hydrogen by the method of positive ray analysis and that of Hogness and Lunn[25] using the same method. These authors conclude that the first ions produced are H_2^+ and that the H^+ ion is produced by collisions with other molecules. Smyth thinks however that the hydrogen molecule ion is energetically unstable with respect to the atom and atomic ion. This would be in disagreement with the theory. Hogness and Lunn think that their experiments are inconclusive on this point. The potentials at which the H_2^+ ion appears are somewhat higher than 14.84 volts though both authors question their absolute values.

No spectroscopic confirmation of the theory has been found up to the present. The theory predicts an ultraviolet limit of 741A. Hopfield[26] found an ultraviolet limit of 885A, which is equivalent to 13.94 volts or 1.030 *Rh*. This would be about the limit to be expected for the molecular spectrum if its ionizing potential is about 14.3-14.5 volts.

[21] Irving Langmuir, J. Am. Chem. Soc. **37**, 417 (1915).

[22] T. Isnardi, Zeits. f. Elektrochemie, **21**, 405 (1915). Wohl corrected a slight error in computation in Isnardi's work. See following reference.

[23] K. Wohl, Zeits. f. Elektrochemie **30**, 49 (1924).

[24] H. D. Smyth, Phys. Rev. **25**, 452 (1925).

[25] T. R. Hogness and E. G. Lunn, Proc. Nat. Acad. Sci. **10**, 398 (1924) and Phys. Rev. **26**, 44 (1925).

[26] J. J. Hopfield, Phys. Rev. **20**, 573 (1922).

The absence of the ultraviolet spectrum of H_2^+ may be due to an extremely low intensity, though if Olson and Glockler can observe the ionizing potentials of the H_2^+ ion, it should be possible to secure the spectrum.

The theoretical work is being continued to see whether it is possible to calculate part of the many lined spectrum of hydrogen by including the contribution of the rotation and vibration of the nuclei to the energy and the change of energy of the electron due to the motion of the nuclei. For the special case of the rotation of the nuclei about the line of vibration of the electron in the vibration orbits, it seems possible to do this without modifying classical mechanics. For the other orbits of the median plane, it seems that some modification of the laws of mechanics must be made.

I also expect to attempt a repetition of the experimental work of Olson and Glockler and possibly some extensions to the resonance states of the ion which should appear theoretically below the ionizing potential of the molecule.

4. The Structure of the Hydrogen Molecule

Since the attempts to calculate the ionizing potential of the helium atom have been unsuccessful, it is very doubtful whether any similar calculations on the hydrogen molecule would be any more successful. But whatever the structure of the normal hydrogen molecule may be, the adiabatic removal of one electron must leave the hydrogen molecule ion in its normal state. If then this normal state of the hydrogen molecule ion is the one suggested here, we can describe the hydrogen molecule as consisting of two nuclei and two electrons, vibrating in approximately straight lines in the median plane between the two nuclei. The two electron orbits may be oriented toward each other at some angle possibly a right angle and may be moving with phases such that the one is at the line joining the nuclei while the other is farthest from this line. Such a model would be diamagnetic. We can speak of such a model only with about the same certainty as we can of the crossed and coplanar models of helium.

The moment of inertia of the hydrogen molecule in its normal state should always be larger than the moment of inertia of the hydrogen molecule in any of its stationary states. When the second electron of the hydrogen molecule is in one of the higher quantum states, the component of its force of attraction on the nuclei in the direction of the line of nuclei would be small and therefore the difference in the moments of inertia of the hydrogen molecule ion and of the hydrogen molecule

in its excited states should be small. In Table IV are given the moments of inertia and distances between the nuclei of the Bohr, Pauli and Niessen and the vibration models of the hydrogen molecule ion and of the excited hydrogen molecule calculated from the Fulcher bands by Allen.[27] These quantities calculated for the vibration model of the ion agree well with those to be expected by comparison with those calculated by Allen for the hydrogen molecule.

TABLE IV

		Moment of inertia (g. cm.^{2}×10^{41})	Distance between nuclei (cm.×10^8)
H_2^+(0,0,1)	(Bohr)	7.05	.921
H_2^+(0,1,1)	(Pauli and Niessen)	72.0	2.942
H_2^+(1,0,0)	(Langmuir and Urey)	2.600	.559
H_2 (First Fulcher Bands)		I_i=1.794	d_i= .462
		I_f=1.862	d_f= .470
H_2 (Second Fulcher Bands)		I_i=1.249	d_i= .385
		I_f=1.292	d_f= .392

Dieke[28] and Takahashi[29] have given very different interpretations to the Fulcher bands than those used by Allen and originally suggested by Lenz.[30] Dieke shows that the so-called Fulcher triplets can be extended and arranges these triplets and other lines as one branch of a band to which he has added another branch. The differences in frequencies which have been usually regarded as due to differences in the rotational energy changes are on Dieke's view to be correlated with vibrational changes in energy. This would make the moments of inertia calculated by Allen entirely meaningless. However, other methods[31] of calculating the moments of inertia as from the heat capacity and entropy give values of the same order of magnitude as those secured by Allen.

This model of the hydrogen molecule also suggests that the non-polar bond of chemists may be regarded as two electrons vibrating in a plane between the two atoms perpendicular to the line joining their nuclei. Such a picture would be a very satisfactory one from the standpoint of chemists, though of course no more so than a similar extension of the Bohr-Debye model of the hydrogen molecule.

[27] H. S. Allen, Proc. Roy. Soc. **106A**, 69 (1924).

[28] G. H. Dieke, Amsterdam Acad. **27**, 490 (1924); Phil. Mag. **50**, 173 (1925); Zeits. f. Physik. **32**, 180 (1925).

[29] Takahashi, Jap. Journ. of Phys. **2**, 95 (1923).

[30] W. Lenz, Verh. d. D. Phys. Ges. **21**, 632 (1919).

[31] See F. Reiche, Ann. d. Physik. **58**, 657 (1919).
E. C. Kemble and J. H. VanVleck, Phys. Rev. **21**, 653 (1923).
H. C. Urey, J. Amer. Chem. Soc. **45**, 1445 (1923).

There are four points of agreement between calculation and experiment which can be regarded as independent: first, the ionization potential calculated agrees with the experimental value and it immediately follows that the calculated values for dissociation and resonance of the atom must agree with these experimental critical potentials; second, the resonance potentials of the hydrogen molecule ion as calculated agree with the experimental critical potentials; third, the heat of dissociation of the hydrogen molecule calculated agrees with the experimental values; and fourth, the moment of inertia of the hydrogen molecule ion agrees with the values expected from the moment of inertia of the excited hydrogen molecule.

My thanks are due to Dr. G. Breit of the Carnegie Institution of Washington for his friendly criticism of this work and for repeating much of the mathematical work and to Dr. E. C. Kemble and Dr. J. C. Slater of Harvard University for their criticism of this paper, and valuable suggestions made in regard to it.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.
October 20, 1925.

BOOK REVIEWS

A Treatise on Light. (Fourth edition). R. A. HOUSTOUN.—The popularity of this standard text is shown by the fact that it has passed through three editions in the last four years. The total changes, however, have been relatively slight and the present edition differs from the last only in the fact that five or six pages in the section on Spectroscopy have been rewritten and a few minor improvements introduced elsewhere. The many friends of the book will welcome, when the time comes a more thorough revision, with the incorporation in the body of the text of material on recent advances such as is now added in a special chapter at the end of the volume.—Pp. xi+486, 334 figs., Longmans, Green & Co., New York, 1925. Price $4.20.

L. R. INGERSOLL

Physikalische und technische Grundlagen der Roentgentherapie. G. GROSSMANN —This book is intended primarily for the radiologist but deals only with the physical and technical aspects of the subject. It contains a comprehensive survey of the field in its present stage of development, particularly as regards German contributions.

The first part of the book is devoted to a general discussion of x-radiation and methods of measurement. Numerous quantitative data are given. The presentation of the dosage problem leaves much to be desired.

The second part is devoted to a discussion of x-ray tubes, high voltage machines and measuring instruments. With two or three exceptions all the apparatus described is of German manufacture. The principles involved, which apply also to American apparatus, are treated extensively.

The subject matter is presented in simple language, using mathematics sparingly and illustrations copiously. The book, therefore, should prove of considerable value to the radiologist. The physicist who wishes to familiarize himself with the problems of x-ray therapy will find it of great assistance.—Pp. viii+300, 207 illustrations, Urban & Schwarzenberg, Berlin, 1925. Price $13.50.

C. G. FAILLA

Über die Synthese der Feldspatvertreter. W. EITEL. Preischriften von der Fürstlich Jablonowskischen Gesellschaft, LII.—The feldspathoids, according to the definition of the author, are a group of minerals closely related to the feldspars in composition and petrogenesis, and thus defined include not only the alkali aluminosilicates such as leucite and nephelite, but also the melilites and the minerals of the sodalite group. The components thus include the common rock-forming oxides Na_2O, K_2O, CaO, MgO, Al_2O_3 and SiO_2, as well as the less common components CO_2, SO_3, S, and NaCl, and it is evident that a comprehensive treatment of the feldspathoids necessitates a discussion of the greater portion of our knowledge of mineral chemistry. Such a discussion has been given, and the author's first-hand experience both in petrology and in physical chemistry has enabled him to give a well-balanced analysis of the material in the literature, which consists of two portions of widely differing character. The first portion comprises the work of the older school, whose mineral syntheses were oftentimes carried out by most ingenious methods, but by methods which bore no possible relation to the natural mineral paragenesis. The second portion includes the precise physicochemical researches of the past two decades, which have yielded much information concerning various binary and ternary systems containing the above common rock-forming oxides. The discussion of this material is particularly full. The third portion of the book

consists largely, of work in which the author has been active, the introduction of volatile components, particularly CO_2, into mineral systems; work which has served to show the physico-chemical relationship of the complex mineral cancrinite and the more usual compounds calcite, sodium carbonate and nephelite. This book is to be recommended to all interested in the problems of mineral chemistry and their study from the standpoint of physical chemistry. The indexing has been well done.—Pp. viii+258, Akademische Verlagsgesellschaft m.b.H, Leipzig, 1925. GEORGE W. MOREY

Photoelectricity. (Second Edition). H. S. ALLEN.—The first edition of Allen's "Photoelectricity," published in 1913, has been almost the only work in English dealing in a comprehensive manner with all aspects of the subject. Since 1913 the subjects of atomic structure and radiation have experienced an extraordinary development which might well be expected to make any text quite out of date, which dealt with phenomena occurring as the result of the irradiation of matter. The author of this book, while recognizing this situation in principle yet finds the facts of photoelectricity and the deductions to be drawn from them substantially unaltered. Another way of stating this might be that the true nature of photoelectric action is no more understood now than then. Proceeding on this basis the size, arrangement and illustrations of the new edition closely follow the old. The first nine chapters describe the early experiments, methods of measurement, the typical phenomena in various types of cells and with various kinds of illumination. These chapters are followed by an interesting series of reviews of allied subjects such as fluorescence and phosphorescence, photography and physiological effects, in which photoelectric action may be considered to play an important part.

A criticism to which the book, being professedly a second edition, is open, is that by its retention of the original illustrations, with exceedingly few additions, the perspective of the presentation suffers. Recent work is not only relatively poorly illustrated, but its description, for lack of appropriate diagrams, is much less thorough and intelligible than is the case with early work. Deletion of portions of the chapter on photoelectric fatigue, now a subject largely of historical interest, elimination of detailed discussion of phenomena which have turned out to be due to poor experimental technique, and more critical discussion of later work in place of the very rapid general review with which much of this is presented, would make the book more valuable to serious students.

The references given are commendably complete, and practically all important work on the subject is given some mention. A full bibliography of papers since 1913, and appendices containing useful constants and relationships enhance the value of the book. It should prove a very valuable book for those who wish an introduction to the subject. —Pp. xi+320, 43 figs. Longmans, Green & Company, New York, 1925. Price $6.50.
HERBERT E. IVES

A Condensed Collection of Thermodynamic Formulas. P. W. BRIDGMAN.—This collection covers the 10 most frequently used variables, with the equations formed from them and their first and second derivatives. The possible number of such equations is very great, too great to be listed in detail. Bridgman has succeeded by a relatively simple classification in reducing the number of equations to be listed so that they are readily printed and correspondingly readily used. To use the tables, this classification must be mastered—a task well worth while, for its comprehensive survey of the group of relations, and the added mastery over them. Solutions for a number of problems are given to illustrate the use of the tables. Workers in this field should find the book of material help both in finding desired relations and in permitting a comprehensive survey of the group of relationships related to the problem in hand.—Pp. 34, Harvard University Press, Cambridge. Price $1.50. J. R. ROEBUCK

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE KANSAS CITY MEETING,

DECEMBER 28, 29, AND 30, 1925

The twenty-seventh annual meeting (136th regular meeting) of the American Physical Society was held at Junior College, Kansas City, Missouri, on Monday, Tuesday and Wednesday, December 28, 29, and 30. The presiding officers were Professor Dayton C. Miller, President of the Society, and Professor K. T. Compton, Vice-President. The attendance was about one hundred and fifty.

On Tuesday afternoon at four o'clock, Professor Dayton C. Miller delivered the presidential address on "The Michelson-Morley Ether-drift Experiment—Its History and Significance," in the Assembly Room of the Junior College. This address was a general session of the A.A.A.S.

The annual joint session with Section B was held on Wednesday morning, with Professor H. M. Randall, Chairman of Section B, presiding. The retiring Vice-President, Professor K. T. Compton, opened the joint meeting with an address entitled "Dielectric Constants and Molecular Structure." This was followed by a symposium on "Relativity," consisting of three addresses as follows: "The Effect of the Earth's Rotation on the Velocity of Light," by H. G. Gale, University of Chicago; "Astronomical Evidence for Gravitational Displacement of Spectrum Lines," by Charles E. St. John, Mt. Wilson Observatory; "Experimental Science and World Geometry," by A. C. Lunn, University of Chicago. In the absence of Professor Gale, owing to illness, his paper was read by Dr. W. W. Watson.

On Tuesday evening, December 29, 1925, there was a dinner for the members of the Society and of Section B and their friends at the Hotel Baltimore, attended by ninety-eight persons.

Annual Business Meeting.—The regular annual business meeting of the American Physical Society was held on Tuesday morning, December

29, 1925, at eleven o'clock. A canvass of the ballots for officers resulted in the elections for the year 1926 as follows:

For President;	Dayton C. Miller
For Vice-President;	K. T. Compton
For Secretary;	Harold W. Webb
For Treasurer;	George B. Pegram
For Members of the Council, Four-year term;	A. H. Compton E. P. Lewis
For Managing Editor of the Physical Review, Three-year term;	John T. Tate
For Members of the Board of Editors of the Physical Review, Three-year term;	J. A. Gray G. E. M. Jauncey J. H. Van Vleck

The Secretary reported that during the year there had been 171 elections to membership, and that the resignations of 54 had been received. The deaths of 5 members were reported during the year. The total membership was 523 Fellows, and 1237 Members, making a total of 1760.

The Treasurer presented his financial report for the year 1925. The Managing Editor of the Physical Review presented the financial report for the year 1925, together with a report showing the progress of the Review during the years 1923, 1924 and 1925.

On motion of Professor R. A. Millikan, the following resolution was unanimously passed:

"*Resolved* that the Physical Society express its appreciation to the retiring Editor of the Physical Review for the following specific reasons:

1. He has introduced an abstracting system which had proved a distinct contribution to bibliographic method and has made the Physical Review in this respect a model already followed by many journals.

2. He has greatly improved the quality of the papers appearing in the Review, by an immense amount of detailed editorial work, and by insisting that contributors present their results with brevity and elegance.

3. He has given a demonstration of value to other sciences in that a journal, which a few years ago seemed unable to run without a subsidy, has been made to do so by attention to brevity and other elements of quality. By these services Dr. Fulcher has made an outstanding contribution to scientific progress."

Meeting of the Council.—At the Meeting of the Council held on December 28, 1925, three persons were elected to Fellowship, one was transferred from Membership to Fellowship, and twenty-six were elected to

Membership. *Elected to Fellowship:* William Bowie, Otto Laporte, H. Nagaoka. *Transferred from Membership to Fellowship:* Kanji Honda. *Elected to Membership:* Penrose S. Albright, Edward V. Appleton, Z. T. Chang, James L. Dunham, H. F. Fruth, R. J. Havighurst, Leland D. Hemenway, Victor Henri, Edward L. Hill, H. J. C. Ireton, Z. N. Loh, Daniel P. Mahoney, Roy H. Mortimer, Suminosuke Ono, Robert H. Oster, Neil B. Reynolds, Carl S. Roys, Richard Rudy, Matthew H. Schrenk, Surain Singh, Hildegarde Strücklen, Clyde H. Tarney, Henry W. Taylor, Tillman G. Titus, Louis J. Waldbauer, Robert G. Wulff.

The regular program of the American Physical Society consisted of 53 papers, Numbers 11, 14, 16, 19, 23, 25, 26, 37, 38, 41, 44, 47, 51 and 52 being read by title. The abstracts of these papers are given in the following pages. An **Author Index** will be found at the end.

HAROLD W. WEBB,
Secretary.

ABSTRACTS OF PAPERS

1. A correspondence theorem for the Compton effect. G. BREIT, Carnegie Institution of Washington.—As has been discovered by Bohr, the frequency emitted by a hydrogen atom as it falls from one of its quantized states to another may be expressed as a properly taken average of the frequency of the electron in its orbit (or of an overtone of that frequency) between the initial and the final state. In the present paper it is shown that the same is true for the Compton effect. The frequency actually scattered is a properly taken average of the frequency which would be scattered on the classical theory as the electron is accelerated from its state of rest to its final recoil condition. Similarly, the intensity scattered in various directions may be represented as a proper average of the intensities scattered on the classical theory. This point of view eliminates the difficulty of a constant correction-factor which has been encountered by Compton and Woo in their explanation of intensity relations.

2. Experimental values on the ratio of the modified to the total scattering of x-rays. O. K. DE FOE, Washington University.—Using the null method described at the Chicago meeting of the Physical Society for measuring the ratio of the modified scattering coefficient s_2, to the total scattering coefficient (s_1+s_2), a determination has been made for copper and carbon. The wave-lengths used ranged from .2A to .7A while the scattering angle was varied from 60° to 120°. The experimental values of $s_2/(s_1+s_2)$ appear to be always less than the values of this ratio as calculated from Jauncey's theory (Phys. Rev., **25**, 314 and 723, 1925), thus agreeing with the result reported by Woo at the Chicago meeting. Further experiments are in progress for the scattering from other substances. It may further be remarked that the rate of decrease of the experimental values of the ratio of $s_2/(s_1+s_2)$ is greater than the rate of change in the theoretical ratio. A possible interpretation of this is that the probability of scattering by an electron depends upon whether or not the difference in energy between the primary and scattered quanta is sufficient to eject the electron from the atom.

3. An experimental test of the Raman and Ramanathan theory of the diffraction of x-rays by liquids. E. H. COLLINS, University of Iowa.—The liquids, ether, water and glycerine were inclosed in small, thin walled glass cylinders at the center of the x-ray spectrometer and the diffraction curve—intensity of diffracted x-rays plotted against

angle from incident beam—was determined by means of an ionization chamber and electrometer and compared with theoretical curves plotted from a formula given by Raman and Ramanathan. Raman and Ramanathan suggest that ether, because of its high compressibility, should give a broad peak in the diffraction curve. The experimental curve is found to have a broad peak. However, the theoretical curve plotted from their formula is found to be sharp due to the fact that the mean molecular distance is found experimentally to be large. The curves for water and glycerine show closer agreement but there is no evidence of the uniqueness of the theory.

4. Photometric measurement of x-ray plates showing the L absorption of tungsten. C. B. CROFUTT, University of Arkansas.—In previous work (Phys. Rev. **24,** 9, 1924) both the absorption and emission spectra of tungsten were photographed simultaneously on the same plate. It has since seemed advisable to make a photometric analysis of the plates showing the absorption bands. The present paper contains an account of this work and includes the photometric curves obtained in the region of the three L absorption bands. The results are in agreement with the previous results. This work was done at the University of Iowa.

5. The intensity of reflection of x-rays by powdered sodium chloride. R. J. HAVIGHURST, National Research Fellow, Harvard University.—The relative intensities of reflection of the Mo Kα doublet from most of the planes between (111) and (8,6,2-10, 2,0) of powdered NaCl have been measured with an ionization spectrometer, using the focusing method of W. H. Bragg, Brentano, Owen and Preston. The powder was pressed into the form of a thin briquet, and adjusted on the crystal table so that the relation $a/b = \sin\alpha/\sin\beta$ was always satisfied, where a and b are the distances from center of crystal table to focal spot and ionization chamber slit respectively; α is the angle between the primary beam and the surface of the briquet and $\beta = 2\theta - \alpha$, where 2θ is the total deviation. The NaCl particles had an average diameter of 8×10^{-4} cm, so small that the effect of extinction (Darwin, Phil. Mag. **43,** 800, 1922) is negligible. The experimental values of the relative intensities were substituted in the equation given by Darwin and A. H. Compton for intensity of reflection and values of $f^2 e^{-b \sin^2\theta/\lambda^2}$ as a function of the distance between planes and of the electron distribution in the atoms, obtained for different values of θ. These values are in fair agreement with those of W. L. Bragg, James and Bosanquet (Phil. Mag. **42,** 1, 1921) obtained from single crystals of rock-salt, after the application to the latter of a correction for secondary extinction.

6. Secondary electrons from iron; critical potentials. H. E. FARNSWORTH, University of Maine.—The magnitude of the secondary electron current from Fe was measured as a function of the primary accelerating potential, 0 to 300 volts. Limiting curves were obtained for two different specimens of Fe after red-heat treatment and for a film of Fe deposited by evaporation. Three different forms of apparatus were used. In all cases the curves show sharp maxima at 1.2 and 7.0 volts with minima at 3.7 and 9.0 volts, and a less sharp maxima and minima at 10.0 and 12.0 volts, respectively. A steady upward trend of the curve begins at 12.0 volts, which is interpreted as an ionization potential. Potentials corresponding to the position of the maxima are interpreted as resonance potentials. Attempts to locate higher critical potentials than the above showed that the positions of slight changes in slope of the curve varied with uncontrollable conditions and with form of apparatus used. These slight changes are taken to have no real significance. Disagreement between these results and those of other observers is mentioned. While previous results for Cu indicate that a layer deposited by evaporation is amorphous, the present results indicate that a similarly formed layer of Fe is crystalline. These experiments were performed at University of Wisconsin last summer.

7. Voltage-intensity relations of mercury lines below ionization. D. R. WHITE and HAROLD W. WEBB, Columbia University.—Using a special four-electrode tube (hot

cathode and three grids) voltage-intensity curves have been obtained in mercury vapor for about twenty lines in the wave-length interval 2500-5800A. The voltage-intensity relationship for each line appears to be primarily a function of the outer energy level involved. This is very clearly shown by two pairs of lines 4358 ($2p_2-1s$), 5461 ($2p_1-1s$) and 2893 ($2p_2-2s$), 3341 ($2p_1-2s$), each pair of which gave voltage-intensity curves practically identical in form. The groups of lines starting at the $3D$, $3d$ and $4D$, $4d$ levels show similarities, though not as marked. Abrupt changes of slope are to be observed in the curves which seemingly correspond to certain critical potentials. The voltages at which the lines first appear agree with theory, as in previous work by Eldridge and by Hertz.

8. Fine structure of the Balmer lines. WILLIAM V. HOUSTON, National Research Fellow, California Institute of Technology.—A Fabry-Perot interferometer can be used to measure these doublets without the usual errors due to overlapping of the components, if the plate separation is so adjusted that the weaker component comes in the middle of the space between adjacent orders of the stronger component. In this way Hα is found to have a wave-number separation of about .31, while Hβ has a separation of about .33. The resolution is such that the difference between these two can be seen by a casual examination of the plates. This is explicable on the theory of Sommerfeld, if it is assumed that the field within the tube is sufficient to suspend the principle of choice and to cause the appearance of those lines corresponding to a change of zero in the azimuthal quantum number. If this is true, the short wave-length component of Hα should be a doublet with a separation of about .05A. While this has not yet been resolved, the line on many plates looks like a close doublet, and further examination will be made with a microphotometer.

9. Duration of radiation excited in hydrogen by 10.2-volt electron impacts. F. G. SLACK and HAROLD W. WEBB.—Using the method already described (Phys. Rev. **24**, 113, 1924) in which high frequency voltages are applied in phase to the grids of the excitation and photo-electric systems of a four-electrode tube, the life of the $2P$ state in hydrogen, excited by 10.2-volt electron impacts was measured. Excitation was produced only in the positive half-cycle and the peak voltage was too low to permit other than the 10.2 radiation. It is improbable that absorption and re-radiation played any part due to the limited amount of dissociated hydrogen. The experimental curve agrees well with that calculated on the assumption that starting at the instant of impact the radiation falls off exponentially. The exponential constant found was $.83\times10^8$ sec.$^{-1}$ Unless the form of these curves is the result of a lag in the photo-electric effect, as seems improbable, the average time τ for an atom lifted to the $2P$ state by electron impact to return to its normal state by the process of emitting λ1215.6 is 1.2×10^{-8} seconds. If the photo-electric lag is effective this is the maximum value of τ. The same results were found for tubes of different dimensions and for pressures from .075 mm to .25 mm.

10. The time interval between the appearance of certain spectrum lines in the visible region. J. W. BEAMS, National Research Fellow, University of Virginia.—The experimental method consisted essentially in a comparison of the time interval elapsing between the appearance of two spectrum lines with the time required for light to travel a measured distance. The spectra of cadmium, zinc and magnesium in the spark in air and the spectrum of hydrogen in condensed discharges at various pressures were studied. The time intervals measured are as follows: In the spectrum of cadmium from the spark doublet 5378,38 to the line 4800 the time interval was 12×10^{-8} sec.; from 4800 to 5086, 1.3×10^{-8} sec.; and from 5086 to 4678, 0.7×10^{-8} sec. In the spectrum of zinc from the spark doublet 4924, 12 to the line 4680 it was 15×10^{-8} sec.; from 4680 to 4722, 2×10^{-8} sec.; and from 4722 to 4811, 1.3×10^{-8} sec. In the spectrum of magnesium, from the spark doublet 4481 to the triplet 5184, 73, 67 it was 8.2×10^{-8} sec. From 4481 of Mg

to 5378, 37 of Cd it was 7.5×10^{-8} sec., and from 5378, 37 of Cd to 4924, 12 of Zn, 9.6×10^{-8} sec. In the spectrum of hydrogen, Hβ appeared first, Hγ second and Hα third.

11. The time interval between excitation and emission for fluorescein. L. G. HOXTON and J. W. BEAMS, National Research Fellow, University of Virginia.—Solutions of fluorescein at concentrations of 2.5×10^{-5} gm per cc were investigated. The exciting light was limited to the spark lines 4481 of magnesium. It was found that the time elapsing between the beginning of incidence and the beginning of fluorescent emission was $(3.2\pm0.3)\times10^{-8}$ sec. for the aqueous solution and $(3.7\pm0.4)\times10^{-8}$ sec. for the alcoholic solution. In the experimental method about half of the beam of exciting light was intercepted by the solution, the other half passing on and returning, after reflections, by a path whose length could be varied, to a point close enough to the point of division to be seen in the same field as the fluorescent light through an optical system (a modification of the arrangement of Abraham and Lemoine) which was, in effect, a shutter electrically operated by the spark discharge. Its time of closing was advanced until the fluorescent light just disappeared from view; then the light path was lengthened until the returning light did likewise. The time interval sought was thus made equal to that required for light to travel a measured distance.

12. Band series in infra-red absorption spectra of organic compounds. JOSEPH W. ELLIS, University of California, Southern Branch.—A series of outstanding absorption bands below 3μ, already attributed to a carbon-hydrogen bond, is shown to fit accurately the non-linear equation, $\nu_n\times10^{-12}=47.37n-0.783n^2$, (1), where ν_n is the frequency and $n=3$, 4, 5, etc. Numerous secondary absorption maxima in the spectra of both the open chain and closed ring types of compounds, containing only carbon and hydrogen atoms, fit the linear equation, $\nu_m'\times10^{-12}=10.71m$, (2), where $m=10$, 11, 12, etc. They are attributed to a carbon-carbon linkage. All other short wave-length bands can be accounted for by simple additive combinations of low frequency members of series (1) and (2), $\nu_c=\nu_n+\nu_m'$. Other members of these three series are identified in longer wave-length spectra obtained by Coblentz and other investigators.

13. The quantum analysis of the rotational energy of certain molecules. RAYMOND T. BIRGE, University of California.—The formulas recently derived for the constants of the molecular law of force enable one to calculate, from data on a set of *vibrational* states, the higher order terms of the *rotational* energy function. This must be assumed an even-powered function of the nuclear momentum m. The rotational energy data may thus be reduced to a theoretically linear equation whose two constants give the most probable values of the moment of inertia I_0 and electronic momentum ϵ. This method was suggested to the writer by E. C. Kemble. The results in the case of CuH give evidence in favor of half-integers for the *resultant* momentum of the molecule, and for the initial excited state alone, require a small value of ϵ (0.0059), which *increases* with m. The variation in ϵ is due presumably to the warping of the electron orbits, caused by the nuclear rotation. This new method uses all of the data, in determining I_0 and ϵ, and to this fact is due its great accuracy. Separate papers give the results in the case of the Swan bands and the AlO bands. In *all* cases the resultant electronic momentum and nuclear momentum are parallel and in the same sense.

14. Molecular constants determined from the Swan bands. J. D. SHEA and R. T. BIRGE, University of California.—Using the method recently developed for obtaining accurate values of the moment of inertia I_0 and electronic momentum ϵ of certain types of molecules, the following results have been obtained for the rotational energy F (in wave-numbers) of the non-vibrating molecule. For the initial state $F=1.7541m^2-6.911\times10^{-6}m^4+1.22\times10^{-11}m^6$, where $m=k-\epsilon=k-(0.0989+1.746\times10^{-5}k^2)$. k is a half-integer and represents the *resultant* molecular momentum. Hence $I_0=15.792\times10^{-40}$.

For the final state $F=1.6295m^2-6.594\times10^{-6}m^4+1.73\times10^{-11}m^6$, where $m=k-(0.0741+0.964\times10^{-5}k^2)$. Hence $I_0=17.000\times10^{-40}$. These constants have been obtained from the middle component of the triplets of the Swan bands. The values of I_0 and ϵ are surprisingly similar to those for the second positive group of nitrogen (known to be due to N_2) and since the HC·CH molecule has the same number of electrons and nearly the same mass as N_2, this *may* be the emitter of the Swan bands, if such a molecule can vibrate and rotate like a dipole. The above values of I_0 should be accurate to 0.10 percent, and replace the previous approximate values (Phys. Rev. **25**, 716, 1925).

15. The combination relation in the λ3064 OH band. WILLIAM W. WATSON, University of Chicago.—The P,Q,R combination which holds for any normal band is not satisfied in the MgH and OH bands, the defect being as great as 34 cm^{-1} at $m=22$ in the 3064 OH band. New measurements have been made on this band, and satellites of the Q lines have been located which, when combined with the main P and R lines, give the required combination. As predicted by Dieke, these satellites are found to be farther from the main lines than those reported by Fortrat. The possible rotational energy levels are considered.

16. Spectroscopic investigation of acetylene, methane and ethylene. FRANK C. MCDONALD, University of Chicago, (introduced by Harvey B. Lemon).—Although an attempt to obtain emission spectra from acetylene, methane and ethylene (in tubes of the Wood type, in tubes using an oxy-cathode, and in mixtures with helium subjected to a wide variety of pressures and methods of excitation) have failed to reveal any bands definitely ascribed to these complete molecules, a new band spectrum has been observed when methane, in a Wood tube, at a pressure of about 2 mm, is excited by a violent disruptive discharge. This spectrum consists of three bands degraded to the red, with heads at 2263, 2367, and 2395A. Their location where the dispersion of the quartz spectrograph is large and their open character make possible a study of their fine structure, which is now in progress and which it is hoped will reveal their relation to other hydrocarbon spectra. Methane and ethylene in tubes 150 cm long with quartz ends, at pressures up to 90 cm show no absorption, while the absorption of acetylene begins at shorter wave-lengths than that reported by Henri.

17. "True half breadth" of absorption lines. THOMAS M. DAHM, University of Idaho.—True half breadth is discussed by Harrison and Slater. (Phys. Rev. **26**, 176, 1925, and **25**, 783, 1925.) While the shape of the T (transmittancy) curve varies with x, the shape of the $\log_e\log_e(1/T)$ curve is independent of x. For infinitesimal x, $\log_e\log_e(1/T)=\log_e(1-T)=\log_e$ (absorption). Hence "true half breadth" may be obtained by measuring the length of horizontal line drawn at distance $\log_e 2$ below crest of $\log_e\log_e(1/T)$ curve, provided there is no general absorption. If k_0, k_1 and k_2 are absorption coefficients at λ_0, λ_1 and λ_2, where $\lambda_2-\lambda_0=2(\lambda_1-\lambda_0)$, $k_0(4k_2-k_1)-3k_1k_2=0$, with no general absorption, assuming Slater's Eq. (9). $K_0(4K_2-K_1)-3K_1K_2=\Delta$, if there is constant general absorption. Reducing each experimentally determined K by amount $K^1=\Delta/(3K_0-4K_1+K_2)$ corrects for general absorption. A new curve of $\log_e\log_e(1/T)$, or of $\log_e k$ which has the same shape, may be plotted and the "half breadth" found graphically, as above. k^1 need not be found by trial as in Slater's method, and C_1C_2 is determined directly from the curve. If general absorption is variable, of amount k^1, $k^1+\alpha$, $k^1+2\alpha$, at λ_0, λ_1, λ_2, $k^1=\Delta-\alpha(7K_0-6K_1-3K_2+6\alpha)/(3K_0-4K_1+K_2+2\alpha)$, α being determined by trial, provided it is small enough not to displace λ_0 too much.

18. The absorption spectra of the vapors of aluminum, gallium, indium and thallium in the ultra-violet. JOHN G. FRAYNE, Antioch College, and ALPHEUS W. SMITH, Ohio State University.—(1) *Absorption in heated vapors.* The metals were vaporized in a graphite tube 15 cm long heated with an oxy-acetylene torch to 2000°C. A tungsten

under-water spark provided a continuous spectrum. *Aluminum.* At about 1200°C the first seven pairs of the first subordinate series were absorbed. The relative intensities disagree with the Bohr theory. No absorption was observed for the second subordinate series. *Gallium.* At a temperature of about 1500°C, 17 prominent lines appeared, including the first four pairs of the first and second subordinate series and the 5th term of the $2p_1-ms$ series. *Indium.* At about 1200°C 18 lines appeared, including the first three pairs of the first subordinate series, the first 5 pairs of the second subordinate series and the 4th term of the $2p_1-md$ series. *Thallium.* At 400°C 4 lines of the $2p_2-ms$ and 4 of the $2p_2-md$ series appeared, widening into bands with increasing temperature. At 800°C lines from the $2p_1$ level appeared as fine absorption lines. (2) *Absorption in the arc.* A bead of the metal was placed in the crater. *Aluminum.* In a 15 amp. arc the lines of the $2p_2-md$ and $2p_1-md$ series, $m=5$ to 11 were completely absorbed. *Indium.* The lines $2p_2-2s$, $2p_2-3d$, $2p_1-2s$ and $2p_1-3d$ were completely absorbed.

19. Interference in a spectrometer with white light and wide slit. H. M. REESE and L. E. PINNEY, University of Missouri.—The ring-pattern from a Fabry-Perot interferometer is focussed upon the slit of a non-astigmatic concave grating spectrometer. With illumination in white light, a series of curved interference fringes is found, as expected, in the focal surface of the spectrometer. It was observed, however, that although the fringes disappear when the slit is widened a little, they reappear if the widening is continued. For slit-widths ranging from zero to 1.5 or 2 mm, 9 or 10 disappearances and reappearances of the fringes can be observed in the green region, and more at shorter wave-lengths. A theory of the phenomenon, involving some approximations, is presented and shown to be in quantitative agreement with the observations.

20. Optical constants of single crystal bismuth. L. H. ROWSE, University of Iowa, (introduced by E. P. T. Tyndall).—The index of refraction and extinction modulus for light traveling parallel to the optic axis were determined by measuring the ellipticity produced by reflection from the cleavage surface of single crystal bismuth. A Stokes analyser was used and readings were taken in the visible spectrum only. The index of refraction rises from 1.05 at 470 $m\mu$ to 1.55 at 670 $m\mu$, while the extinction modulus rises from 2.7 at 470 $m\mu$ to 3.6 at 670 $m\mu$. The computed reflectivity lies between 65 and 70 percent. The results are compared with those of other observers made on polished surfaces.

21. Optical constants of molybdenite in the ultra-violet. ALFRED W. MEYER, University of Iowa, (introduced by E. P. T. Tyndall).—The index of refraction and extinction index for light transmitted parallel to the optic axis in crystals of molybdenite were determined by measurements of the ellipticity produced by reflection at a cleavage surface. Minor's method was used. The index of refraction rises to a maximum of 7.8 at 480 $m\mu$ and falls to 2.7 at 330 $m\mu$. The extinction index rises steadily from 0.35 at 500 $m\mu$ to 1.0 at 360 $m\mu$ and remains constant to 330 $m\mu$. The reflectivity is computed and compared with results of other observers.

22. Luminescence of Grignard compounds in magnetic and electric fields. R. T. DUFFORD, DOROTHY NIGHTINGALE, and L. W. GADDUM, University of Missouri.—The writers in co-operation with several other workers, have investigated the effects of electric and magnetic fields on the luminescence of organo-magnesium halides in ether solutions. In magnetic fields of the order of 15,000 gauss, the luminescence due to oxidation in air or oxygen is found to be notably brighter in the more intense part of the field. Polarization of the light appears to be nearly if not completely absent. It is impossible to apply large electric fields, on account of the abnormally large conductivity of such solutions. With voltages up to 1500, it is found that the compounds that give luminescence on oxidation with O_2 give light at the anode, but the brightness is not in the same order as with O_2. Polarization appears to be absent here also.

23. On the spectroscopic examination of the striated discharge in mixed gases. DAVID A. KEYS and M. HOME, McGill University.—Continuation of the work on the striated discharge in hydrogen (Trans. Roy. Soc. Canada, **19**, 143, 1925) using the same apparatus but mixtures of (1) hydrogen with helium and (2) hydrogen with nitrogen gave the following results. In the mixture of helium and hydrogen, the Hα line is hardly visible in the negative glow but strong in the striation. The Hβ line, however, is easily visible in the negative glow, i.e., its intensity is stronger than Hα, but in the striation it is weaker than Hα. With a mixture of nitrogen and hydrogen, the Hα and Hβ lines are strong in the negative glow but not detectable in the striation. This is the reverse of what was found in helium and hydrogen. When only hydrogen is used, the Hα and Hβ lines are stronger in the negative glow than in a striation.

24. Resonance potentials in gallium and indium vapors. C. W. JARVIS, Ohio Wesleyan University, (introduced by Alpheus W. Smith).—The critical potentials of gallium and indium were investigated by the methods of inelastic impact. The tube containing the vapors was the differential type used by Hertz but so arranged that by making the proper electrical connections it could be used as a simple three-electrode tube. The three following methods were employed to detect direct ionization: (1) the change of the negative space charge, (2) the Lenard method, (3) the modification of the gap resistance. The results obtained for gallium are: (1) $3.06 \pm .05$ volts. This resonance potential corresponds to λ4033 A and the transition $2p_2 - 2s$. (2) $4.22 \pm .05$ volts which corresponds to λ2874 A and the transition $2p_2 - 3d_2$. In gallium there was evidence of weak ionization at about 6 volts and a stronger second ionization at about 13 volts. Two resonance potentials were also observed for indium. They are as follows: (1) $3.03 \pm .05$ volts corresponding to λ4102 A and the transition $2p_2 - 2s$. (2) 4.07 ± 05 volts corresponding to λ3039 A and the transition $2\ p_2 - 3d_2$. In indium as in the case of gallium there was evidence of weak ionization at about 6 volts and a stronger second ionization at about 14 volts. The failure to get satisfactory ionization for these metals at the voltage corresponding to the first ionization potential is attributed to the small vapor pressure at the temperature used in these experiments, namely 500° to 600° C.

25. Low voltage arcs in iodine. H. F. FRUTH and O. S. DUFFENDACK, University of Michigan.—Low voltage arcs in monatomic and molecular iodine were investigated together with their spectra. From a study of the current-voltage characteristics it was concluded that 6.5 volts is the minimum radiating potential of the atom, 8.0 the ionizing potential of the atom, and 9.5 the ionizing potential of the molecule. Non-oscillating abnormal low voltage arcs were maintained down to 4.9 volts and oscillations were observed around 12 volts. With arc currents of about 2 amperes the filament current could be cut off and the arc sustained indefinitely at 30 volts or above. The spectrum of the 4.9 volt arc contained only 3 lines, ($\lambda\lambda$2062, 2535, 3135) the continuous band 3460, and several groups of bands. At slightly higher voltages arc lines appear and at 8 volts the strongest spark lines begin. These lines are succeeded by new ones at higher voltages making it seem probable that the stripping of the atom is in progress. Peculiar behavior of the lines 2535 and 3135A was observed. Three continuous bands (at 4080, 4300, 4800A) are present in molecular but disappear in atomic iodine. A band system lying between 2224 and 2050A was observed, and two groups of four bands each were found at 2880, 2833, 2776, 2716A and 2480, 2379, 2290, and 2243A.

26. The magnetic properties of atomic rays of the alkali metals. JOHN B. TAYLOR, University of Illinois, (introduced by Jacob Kunz).—The direct experiments of Gerlach and Stern on space quantization with atomic rays of silver, have been repeated in a simplified apparatus. A broadening of the atom stream was found, rather than the actual splitting which Gerlach and Stern were able to detect. The splitting would probably be obtained with narrower slits. Work is now in progress on the alkali metals.

In order to insure deposition of the alkali metal to form an image of the slit, it is necessary to cool the plate with liquid air. Preliminary results on sodium indicate a broadening of the image by a magnetic field as in the case of silver, but the effect obtained so far is too small to establish the conclusion beyond doubt.

27. Conductivity of activated nitrogen. PHILIP A. CONSTANTINIDES, University of Chicago, (introduced by H. B. Lemon).—The conductivity in activated nitrogen produced by an electrodless discharge has been directly measured. Nitrogen gas moving with a uniform velocity has been activated in a bulb, and then passed in an ion chamber consisting of a metal tube charged to suitable potentials with respect to an electrode along its axis connected to an electrometer. The ion current when plotted as a function of the cylinder potential follows Ohm's law to the neighborhood of saturation potential. By increasing the potential beyond the saturation potential an increase of ion current is observed in the vicinity of the ionization potential of N_2.

28. Theory of the cathode of an arc. J. J. SLEPIAN, Westinghouse Research Laboratory, East Pittsburgh.—It is generally believed that thermionic emission at the cathode is essential for the maintenance of an arc, although a number of serious objections have been raised against this view. K. T. Compton has explained the conductivity of the positive column in an arc by thermal ionization of the gas. The author shows that this hypothesis of thermal ionization of the gas may also explain the passage of current to the cathode so that liberation of electrons from the cathode is not necessary, the current being carried to the cathode by positive ions. Quantitative calculations by equations of Saha and Langmuir give reasonable values for the temperature of the gas.

29. The positive ion emission from a mixture containing Fe, Al and Cs, and the work function φ_+ for Cs from this mixture. C. H. KUNSMAN, Fixed Nitrogen Research Laboratory, U. S. Department of Agriculture.—A mixture consisting of magnetite to which about 1% of Al-oxide and about ½% Cs in the form of caesium nitrate was fused in a resistance furnace, where the material itself was the resistor. This mixture furnished a very definite source of positive ions when used as a hot anode in a vacuum. The magnitude of the ion current depended upon the previous gas treatment and state of reduction of the material. After a thorough degassing and glowing in a vacuum, the positive ion current was sufficiently constant at a given temperature so that a very definite and reproducible value of the work function, $\varphi_+ = 2.37$ volts, was obtained by means of Richardson's equation $I_+ = AT^{\frac{1}{2}}\epsilon^{-\varphi\epsilon/kT}$ for temperatures from 962° to 1185°K. That this emission was largely positively charged ions of Cs was determined by the electron emission characteristics of a tungsten filament, placed so as to collect some of the positively charged particles. The reduced mixture of the oxides of Fe, Al and Cs is a good catalyst for the synthesis of ammonia from N_2 and H_2.

30. Departures from Ohm's law and theories of metallic conduction. K. T. COMPTON, Princeton University.—Four years ago Bridgman reported departures from Ohm's law of the order of one percent for current densities of the order of 10^6 amp. per cm² in gold and silver. It is shown that such departures render untenable Thomson's "second" (or doublet) theory of conduction, but are of the order to be expected on the classical free electron theory. The classical electron theory expression for conductivity is used, except that account is taken of the fact that the electrons are not in thermal equilibrium with the atoms but have greater energies on account of the field. These energies are calculated after the manner of "terminal" energies. The electronic free path can be calculated from the experimental data by

$$l = (\alpha T/Ee)[(9.072m/M)(\sigma - \sigma')/\sigma]^{\frac{1}{2}}$$

where σ and σ' are the conductivities at low current density and with potential gradient E, respectively, m and M are electronic and atomic masses and αT is the mean kinetic

energy of the atoms. The free path l comes out $2.85(10)^{-4}$ cm for gold, a value consistent with other indications. Critical experimental tests of the theory are suggested by the equations.

31. The resistivity of liquid alloys. C. V. KENT, Kansas University.—The expression $\rho=2mW/Ne^2$ for the resistivity ρ of a metal (W being the free electron impact frequency and N the free electron density) in the simple electron theory, is consistent with electrical and optical data for molten metals and alloys (C. V. KENT, Phys. Rev. **14**, 459, 1919, and **23**, 479, 1923). W and N seem to be linear functions of the atomic or molecular percent of one component in the alloy, or of one component in the component-compound alloy when such compound (or aggregate) is indicated by the melting point diagrams. The atomic concentration-resistivity graph should then be one or more sections of rectangular hyperbolae. This conclusion has been tested from the data of others and for some obtained by Mr. Geo. Emery and the writer, and is apparently confirmed. Furthermore the free electron concentration is independent of the temperature, the entire temperature change in resistivity being due to the variation in the free electron impact frequency with the temperature. The data available are generally insufficient and further experimental work is in progress. There is some evidence that the resistivity curves of some solid alloys obey the same laws.

32. The location of the electromotive forces in galvanic cells and thermocouples. W. H. RODEBUSH, University of Illinois.—Electromotive forces may be classified as (1) electromagnetic, (2) electrostatic, (3) electrokinetic. In the galvanic cell the conclusion is drawn that the principal e.m.f. resides at the junction of electrode and solution. There is neither an e.m.f. nor a difference of potential of appreciable magnitude at the metallic junctions. In the thermocouple the e.m.fs. are electrokinetic. The second law of thermodynamics does not indicate the location of these e.m.fs. but the first law requires them to be associated with heat effects. In a thermocouple with infinitesimal temperature difference between junctions these e.m.fs. are to be referred to the junctions. This conclusion can be extended to cases where a finite temperature difference exists.

33. Experiments with standing electromagnetic waves produced by means of a short wave electron tube oscillator. ALEXANDER MARCUS, College of the City of New York.—For laboratory experiments with electric waves about two meters in length, the following type of short-wave generator has been found convenient. A linear oscillator adjustable to a length of about one meter is energized by means of an oscillating circuit consisting of a single turn of wire about four inches in diameter, with its ends connected to the grid and plate respectively of an ordinary electron tube like the 201A type. The wire is broken at its midpoint and a variable condenser having a maximum capacity of 0.0001 mf is inserted for the purpose of facilitating the tuning of the closed driving circuit to the fundamental wave-length of the linear oscillator. The latter has a hot-wire meter at its center to indicate the production of a current antinode at resonance. The polarized waves radiated by the linear oscillator may be conveniently detected by means of a similar linear oscillator with a thermal galvanometer inserted at its middle point. With the help of a grid of several parallel wires it is easy to produce standing waves having prominent nodes and loops in a room of ordinary size. A pair of Lecher wires loosely coupled to the driving circuit affords a check method of measuring the wave-length.

34. Application of a vacuum tube multimeter to electrical measurements at radio frequencies. S. LEROY BROWN and M. Y. COLBY, University of Texas.—The usual low frequency voltmeter-ammeter methods of measurements can be extended to include audio and radio frequencies by the use of a vacuum tube meter utilizing two triodes. The grid potential of the first tube is lowered proportionally to the peak value of the

applied voltage; this decreases the plate current of the first tube and the direct potential drop across a high resistance in its plate circuit is so applied in the grid circuit of the second tube that the result is an increase in the plate current of the second tube which is measured by a direct current micro-ammeter. This instrument is so constructed that its input impedance is very high, it is independent of the nature of circuit to which it is connected and its registration is independent of frequency up to a million cycles per second. The lowest measurable electromotive force is about .05 volts and, therefore, with a non-inductive resistance of 1000 ohms, a current of 50 micro-amperes can be measured. Other applications of the instrument are: testing of audio and radio transformers, measurement of induced electromotive force in loop aerials and the intensity of harmonics, and the detecting of bridge balance.

35. Accurate measurement of small capacities. WILLIAM SCHRIEVER, University of Oklahoma.—The capacity of an electrometer and its connections may be obtained by the usual condensers-in-parallel method but the results will not be accurate unless the capacity of the shielded connecting wire is taken into account. By connecting each of two cylindrical condensers (alike in every respect except length) to the electrometer system in exactly the same way, it is possible to eliminate the "end-effects" in the calculations. These "end-effects" include the errors due to the finite length of the condensers (formula for capacity of concentric cylinders per unit length assumes them to be of infinite length), the errors due to the presence of insulating material between the parts of each condenser, and the errors due to the capacity of the wire connecting the condensers to the electrometer system. A constant source of ionization is required.

36. Measurement of the high frequency resistance of coils. R. R. RAMSEY, Indiana University.—The high frequency resistance of a coil is measured by comparing the heat (I^2R losses) produced in the coil by a radio frequency current (10^6 cycles) to the heat produced by a d.c. current in a known resistance. A differential thermometer is made of two inverted Pyrex beakers cemented to glass plates. Through each glass plate two electrical connections and a glass tube are cemented. The glass tubes are connected to a U-tube half filled with water. The coil to be measured is placed in one beaker and the known d.c. resistance is placed in the other. The heat developed in the two coils as indicated by the water in the U-tube is made equal by varying the d.c. current. The high frequency resistance of the coil is found to be less than that found by measuring the resistance of the circuit by the usual method in which the resistance of the condenser is assumed to be negligibly small. With a constant frequency the difference increases with the inductance of the coil.

37. The variation of the resistance of condensers with dial setting at radio frequencies. A. E. MAIBAUER and T. SMITH TAYLOR, Bakelite Corporation.—In the measurement of the power factor of insulating materials by the resistance variation method, or by the substitution method, it has been customary to consider the resistance of the standard condenser as negligible compared with that of the sample under test. The writers were aware of the fact that this assumption was not justified and have determined the values of the effective series resistance of two condensers used as standards in power factor measurements. Use was made of a standard condenser made from two adjustable parallel plates. This condenser having either nothing but air, or very small pieces of Pyrex glass or mica as dielectric had as small an effective resistance at 1,000,000 cycles as it was possible to obtain. Curves are given which show how the resistances of condensers vary with dial settings.

38. A new type of electromagnetic wave-meter. W. W. SALISBURY, University of Iowa, (introduced by C. J. Lapp).—A high degree of accuracy and sensitivity are obtained by using a combination of a two element vacuum tube and direct current

galvanometer, which measures the voltage across the condenser in the resonant circuit instead of the current in the inductance as is the common practice. The small amount of energy necessary to operate this indicator makes possible a very sharp resonance peak. Its sensitivity allows it to be operated so far from the source of the waves that it does not effect the wave-length. A new method of locating nodes on Lecher's wires makes possible greater accuracy than has previously been obtained in such measurements. The wave-meter is calibrated, with the aid of these wires, for wave-lengths between 3 and 100 meters.

39. An electrical frequency meter of wide range. HOMER L. DODGE, University of Oklahoma.—The paper describes a direct-reading, electrical frequency meter of wide range made up of standard electrical laboratory equipment consisting principally of condensers and an a.c. milliammeter.

40. Dielectric constant of helium and oxygen in a magnetic field. B. B. WEATHERBY and A. WOLF, University of Pennsylvania.—The heterodyne beat method was used to detect a possible change in the dielectric constant of gases, due to space quantization in a magnetic field. A condenser, forming a part of one oscillating circuit of about 1,000,000 cycles frequency, was filled with the gas investigated and the magnetic field then applied. The results obtained show that for helium (20 cm pressure), air (76 cm) and oxygen (76 cm) at room temperature there is no change in the dielectric constant to 1 part in 500,000. The magnetic field was of the order of 8000-10,000 gausses, while the electric field was estimated at 5000-10,000 volts/cm. The tests were carried out with the direction of the electric field both parallel and normal to the direction of the magnetic field. This work was suggested by theoretical considerations in an article by Ruark and Breit (Phil. Mag. Feb. 1925).

41. Effect of deposition-temperature on the magnetic properties of evaporated nickel films. R. L. EDWARDS, University of Iowa.—Uniform nickel films of thickness $30m\mu$ to $300m\mu$ were produced by evaporation on an aluminum foil base. Deposition occurred at temperatures ranging up to 250°C with a vacuum in most cases better than .003 mm. The magnetic properties were quantitatively determined with fields up to 139 gauss. Films deposited on an unheated surface were found to be only slightly magnetic, but for such films, the coercive force was also very small. The effect of maintaining films at a relatively high temperature during deposition was to greatly increase the permeability for large fields, and to increase the coercivity in a still greater ratio—that is, to increase both dimensions of the hysteresis loops. Loops plotted on the same scale of magnetic induction and field strength varied in area more than ten-fold due to this cause. Areas more than eighteen times as great as for annealed bulk metal were obtained. Presumably the films were crystaline, and their formation on a heated surface would produce larger crystals, yet such films were harder physically as well as magnetically than those produced on unheated surfaces.

42. Thermo-electric power and the Hall coefficient. C. W. HEAPS, Rice Institute.—The simpler theories of free electrons in metals make the Hall coefficient depend only on electron concentration. The thermo-electric power of a couple depends on the ratio of electron concentrations in the two metals. A relation between Hall coefficient and thermo-electric power is thus to be expected. Experiments performed on Bi and Sb show a Hall coefficient decreasing as the magnetic field increases while the thermo-electric powers of these metals with respect to copper increase. For crystalline graphite, increasing the magnetic field increases the Hall coefficient and decreases the thermo-electric power. No other non-magnetic metals have been found to have a variable Hall coefficient or thermo-electric power (with the possible exception of Te) so the tentative rule may be stated: If the Hall coefficient of a non-magnetic metal varies

with the field the thermo-electric power of that substance will be found to vary in a converse way with the field. Richardson has suggested that any cause producing a continuous alteration of electrical conductivity at a given temperature should produce a corresponding alteration of the thermo-electric power. A magnetic field acting on graphite does not appear to behave in accordance with this suggestion.

43. A "Node" at the source. G. W. STEWART, University of Iowa.—Current literature shows a fairly general misunderstanding concerning the nodal location of the vibrating source in the Kundt's tube and in the Melde transverse string and fork experiment. It is shown by theoretical deduction that this source is one-half wave-length from the nearest node, that it is located more correctly *at a node* than "near a node" or "practically at a node." Experimental justification is also cited. The motion of the source is the cause of the misunderstanding, but the source, a boundary between two media, has a displacement that is exceedingly small compared to a wave-length and reflects and permits stationary waves to form just as if it were stationary.

44. Measurement of air velocity by means of a Rayleigh disk. C. N. WALL, University of Illinois, (introduced by F. R. Watson).—A Rayleigh disk was suspended by means of a quartz fiber in a pipe through which flowed a uni-directional stream of air from a constant pressure tank. By independent measurements of the air velocity and the resulting torque exerted upon the Rayleigh disk an empirical relation between the two quantities was established. It was found that the torque exerted upon the disk by the air stream is proportional to the 1.7 power of the air velocity instead of to the square of the velocity as predicted by the classical theory.

45. The vapor pressure of solid potassium amalgams. FRANKLIN E. POINDEXTER, Washington University.—A Buckley ionization gauge was used to measure the vapor pressure of three potassium amalgams ranging in concentration from 5 : 1 to 15 : 1 mol ratio of Hg to K. The vapor pressure of each amalgam was measured at a number of temperatures which were determined by means of a platinum resistance thermometer. The pressures measured varied from approximately 10^{-6} mm to 10^{-3} mm over a maximum temperature range of from -24°C to 28°C. The log p vs $1/T$ graphs for the different amalgams were found to be approximately straight lines. The heats of reaction were calculated by means of the Van't Hoff reaction isochore, the pressures at different temperatures for these calculations being taken from the log p vs $1/T$ graphs. These heats were of the order of 25,500 cal. per gram molecule of amalgam. The corresponding heats of reaction for sodium amalgams, as reported at the Chicago meeting of the Physical Society, were found to be of the order of 14,500 cal.

46. The relative importance of the Bernouilli principle and of viscosity in aspirator action. E. L. HARRINGTON, University of Saskatchewan.—Although the Bernouilli principle is cited in most text books of physics as the complete explanation of aspirator action it is found from both theoretical considerations and experimental study that the viscosity of air is really by far the more important factor to be considered. Aspirators designed to more thoroughly utilize the latter are described and shown to be many times as efficient as those designed to utilize only the Bernouilli principle.

47. Measurements on the thermal expansion of fused silica. WILMER SOUDER and PETER HIDNERT, Bureau of Standards.—Expansion tests were made on transparent and non-transparent fused silica over various temperature ranges between -125° and $+1000$°C. Seventeen samples of fused silica were examined on which a total of 48 expansion tests were made. A detailed description of the apparatus and the methods used in this research and a summary of available data obtained by previous observers on the thermal expansion of fused silica are given. A critical temperature or minimum length was found at about -80°C. Expansion occurred on heating fused silica above the

critical temperature or on cooling below this temperature. Typical expansion curves are shown and discussed, and the authors' average expansion curve compared with the results of previous investigators. The following table gives average coefficients of expansion derived from the data on all samples for various temperature ranges.

Average Coefficients of Expansion per Degree Centigrade of Fused Silica.

20 to 60°C : 0.40×10^{-6}	20 to 600°C : 0.53×10^{-6};
20 to 200 : .50;	20 to 750 : .50;
20 to 400 : .55;	20 to 1000 : .48.

48. Piezo-electric effect in sodium bromate. JOSEPH VALASEK, University of Minnesota.—The general problem of deduction of physical properties of crystals from their structure and kinds of atoms is a difficult one for which there may be some possible simplifications. Certainly, however, the replacement of the ions in sodium chlorate and bromate by point charges, leaves much of their piezo-electric moment unaccounted for. Experimentally, it is found that the change in the lattice constant of sodium bromate with temperature, which is given by the coefficient of thermal expansion, is 0.0000286, while the temperature coefficient of the piezo-electric constant is roughly one hundred times as large. This is entirely out of proportion to the change one would expect from a simple expansion of all atomic distances. By using different temperatures one can obtain the same piezo-electric constant from the sodium chlorate and bromate. This requires only a reduction of the bromate lattice by 10 percent of the difference between the two, that is, the bromate must be about 100°C cooler than the chlorate. The data show that the use of point charges instead of the ions in the crystal lattice cannot give correct results, and show the magnitude of the discrepancy. Details will be published later.

49. Thermodynamics of thermionic phenomena. N. RASHEVSKY, Westinghouse Research Laboratory, East Pittsburgh, (introduced by Dayton Ulrey).—An attempt is made to reduce all thermodynamical treatments of thermionic phenomena to the most general and exact form. In connection with this the kind of assumptions and approximations underlying all the thermodynamical methods used at the present time are investigated. Special attention is given to the rôle of the positive ions in the solid as well as in the gaseous phase and their possible mutual interaction with the electrons. Using the outlines of this general method, results obtained in a previous paper (Zeits. f. Phys. **33**, 606, 1925) as to the influence of pressure and the rôle played by the chemical constant of the emitter are confirmed, and furthermore are shown to be independent of the special assumptions made in that paper. In connection with a recent paper by W. Schottky the question is discussed as to whether the law of emission is the same for all substances or whether it may be different for elements and compounds.

50. Simple demonstration of the constancy of mass. J. A. ELDRIDGE, University of Iowa.—The content of the electromagnetic field equations is very nearly the same as that of restricted relativity. It is well known that many of the results of relativity were obtained much earlier by electromagnetic reasoning. The purpose of this paper is to show as simply as possible the variation of mass with speed and to make the mass concept more concrete. The relation between the charge and the Faraday tube of force is like that between a spider and its thread—the tube of force furnishes not only the accelerating force but also adds to the mass moved. The charge, if accelerated in the direction of its velocity, adds to itself a Faraday tube; a transverse (i.e. centripetal) acceleration means no accumulation of mass. These concepts give numerically the variation of mass with velocity and the difference between longitudinal and transverse mass. This picture of the diffuse stationary mass being absorbed by the denser moving mass is quite general and illustrates the general principle of conservation of mass.

51. An oscillographic study of atmospherics. ROY H. MORTIMORE, University of Iowa, (introduced by E. P. T. Tyndall).—The variations of potential accompanying lightning flashes induced current in a critically damped antenna. The potential across a series condenser in the antenna was amplified with a resistance coupled amplifier the output of which was connected to a Duddell oscillograph. The photographic records obtained show that the impulses are unidirectional, aperiodic, and vary in duration from 500 to 8000 micro-seconds.

52. The energy levels of the carbon monoxide molecule. RAYMOND T. BIRGE, University of California.—It is possible to arrange all of the fourth positive group of carbon, and also Lyman's "fifth positive group" and nearly all the remaining previously unassigned bands in one quantum system of some 150 bands, given by $\nu = 64{,}721 + (1499.28n' - 17.24n'^2) - (2147.74n'' - 12.703n''^2)$, where n' varies from 0 to 14, and n'' from 0 to 22. The distribution of intensity is a typical one, similar to that for the aluminum bands. The expected portion of these bands has been found by Leifson in absorption in cold carbon monoxide, and this system therefore represents the fundamental "resonance" system of CO. The Angstrom CO bands have as a final state the initial state of this same system. Duncan has unknowingly measured the excitation potential of the first negative group of carbon (due to CO^+), from which one obtains 14.2 volts for the ionization potential of CO. Therefore the relative energy values of three electronic levels for CO, and three for CO^+ are now known, and also the excitation potential for the fourth group of carbon (8.0 volts, "resonance potential"), Angstrom CO bands (10.7 volts), comet-tail bands (16.7 volts), first negative carbon bands and the "combination bands" of CO^+ (19.8 volts).

53. The structure of molecules. RAYMOND T. BIRGE, University of California.—Recent developments in band spectra indicate that there are in diatomic molecules electronic energy levels which may be designated *s*, *p*, etc., and which have a multiplicity similar to that of a certain "corresponding" atom. New quantitative examples of this are given for CO, N_2 and NO. The results for CO (previous abstract), together with those for N_2, H_2 and He_2, indicate that these molecular levels are given also at least approximately by the *formulas of line spectra*. Hence the structure of the outer electrons of molecules must be very similar to that of the "corresponding" atom (CO and N_2 like Mg, CO^+ and N_2^+ like Mg^+, CN and BO like Na, NO like Al, etc.), as already suggested by Mulliken and Mecke. Moreover, in CO, CO^+, NO, CN and BO, the frequency of vibration of the dipole is less, and consequently the moment of inertia is greater, when the radiating electron is in a *p* level, than when in any *s* level. This seems to be evidence that the radiating electron moves in a protruding path, to give the valence properties, which also penetrates to varying degrees the region *between the two nuclei*, and so plays a definite role in determining the strength of the chemical bond.

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